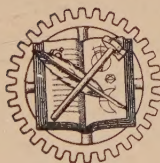


METALLURGY OF WHITE METAL SCRAP AND RESIDUES

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BY

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PREFACE

In spite of the rapidly growing importance of the scrap and residue treating industries, American metallurgical literature contains very few exhaustive monographs or articles, and not a single work on this subject. A small handbook on the treatment of residues was published in England more than 10 years ago, while another monograph on the metallurgical treatment of scraps and residues was published by myself in German script two years ago.

It has been my endeavor in this volume to give all the elementary as well as the important facts directly and indirectly related to the metallurgical treatment of all white metal wastes, including the zinc and aluminum materials, particular attention having been paid to the condition and requirements of small and medium sized plants, operating independently or in connection with large manufacturing or engineering concerns working up their own scrap and residues. Allied subjects such as engineering construction matters, mechanical apparatus used for transportation, briquetting, blast furnace operation, etc., have been treated in a generally descriptive way. Those seeking more detailed information on these subjects are referred to special works on general metallurgical topics such as Hoffman's "General Metallurgy."

Being the first comprehensive publication on the metallurgical treatment of scrap and residues, this volume does not claim to be an encyclopædia on this subject. It is possible that one or the other important matter, which has not come to my attention, may have been omitted while other subjects of lesser interest to the majority of readers have been accorded too large a space. Constructive criticism is cordially invited, and suggestions concerning the treatment of individual subjects, or the editing of this book in general, will gladly be evaluated should the interest shown in this work justify the preparation of a second edition.

Acknowledgment is due Messrs. Robert J. Snelling and Karl B. Thews for the execution of a number of drawings contained in this volume.

EDMUND RICHARD THEWS.

Philadelphia, Pa.
October, 1929.

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METALLURGY OF WHITE METAL SCRAP

INTRODUCTION

One of the most important factors influencing the development of the metal industries of the world is the steady advancement achieved in the organization of the metallic scrap and residue trade and in the mechanical, chemical, and metallurgical treatment of these materials. Due to the enormously increased production and consumption of metals within the last twenty-five years and to the correspondingly rapid accumulation of metallurgical and industrial wastes, efficient recovery of these products has become an important economic necessity, and the development of this branch of the metallurgical arts represents a problem which, in view of the manysidedness of the processes involved and on account of the ever-changing industrial conditions, is hardly equalled by the technical difficulties encountered by any related industry.

The rapidly growing importance of the scrap and residue industry is most convincingly reflected in the increase of volume and value of non-ferrous scrap and residues handled. Thus, from 1918 to 1925, the production of secondary lead, zinc, and aluminum increased by 175, 125, and 190 per cent respectively, that of copper increased by 60 per cent, while the respective figure for tin, 11 per cent, is by far the lowest for the commoner metals.

Since 1921, when lessened consumption and lower prices reduced the value of the important secondary metals recovered to less than half that of the previous year, recovery of scrap and other non-ferrous metallurgical wastes has increased constantly from year to year. The relative decrease in recovery effected in 1924 did not affect the recoveries of secondary lead, tin, antimony, and aluminum, but was confined to copper alloys and zinc alone.

The recovery of the important non-ferrous scrap materials in the United States from 1920 to 1926 is given in the following table:¹

¹ Bureau of Mines, "Secondary Metals."

QUANTITY OF IMPORTANT SECONDARY METALS RECOVERED FROM 1920 TO 1926
(In 1000 Short Tons)

	1920	1921	1922	1923	1924	1925	1926
Copper, including that in alloys other than brass.....	130.6	113.4	144.1	193.2	196.5	250.6	281.7
Brass scrap remelted...	259.8	148.5	274.0	311.0	274.0	242.3	283.0
Lead as metal.....	56.4	46.4	75.5	96.4	90.4	112.4	125.0
Lead in alloys.....	68.3	57.4	84.1	98.1	114.1	114.5	152.3
Zinc as metal.....	42.9	33.8	69.3	65.2	58.9	61.4	64.6
Zinc in alloys other than brass and in chemical compounds.	7.7	5.8	10.3	8.6	10.5	13.3	13.4
Tin as metal.....	7.2	5.4	6.6	7.9	7.7	8.0	9.8
Tin in alloys and chem- ical compounds.....	16.3	11.5	12.9	22.3	23.6	23.0	23.7
Antimony as metal....	.2	.03	.2	.2	.09		2.9
Antimony in alloys....	5.4	4.7	6.9	7.8	9.3	10.8	13.3
Aluminum as metal....	5.0	3.7	7.2	6.8	10.4	17.7	20.5
Aluminum in alloys....	10.5	5.3	9.1	14.5	16.7	26.3	23.7

During the year 1927 and the first part of 1928 conditions remained fairly constant, while the latter part of 1928 was characterized by considerable progress in business and along technical lines. The general outlook for the next few years appears to be similarly favorable, although the ever increasing competition will force scrap and residue dealers as well as smelters to make still greater efforts towards improving their organizations and increasing the efficiency of their operating processes.

The problems facing the metallurgical scrap and residue industries are not limited to the rational evaluation of scraps and residues alone, of course, but include the elimination of unnecessary waste in production, distribution, and consumption as well. The general movement for the elimination of waste in production has become of steadily increasing importance throughout the world, and the policies adopted by the interested societies and authorities in the various countries gradually drift into uniform channels, the experience of one group serving to determine or modify the policies of the others.

In this country, the problem of elimination of industrial waste

was accorded national recognition in 1921, when a Committee of 17 prominent engineers was appointed by Herbert Hoover, then President of the Federated American Engineering Societies, to engage in an extensive study of the causes of waste then prevalent in American industry. This Committee found that among the six major industries investigated, the waste in the metal trades amounted to 29 per cent.

One of the most important means of eliminating or, at least, reducing this enormous waste is the simplification and standardization of metallurgical and engineering products, a movement most ably supported by the Department of Commerce under the leadership of Herbert Hoover. This effort at simplifying and standardizing metallurgical products is becoming increasingly noticeable in practically all branches of the alloying industry. Thus, according to investigations carried out by the U. S. Bureau of Mines, about 97 per cent of all aluminum castings now made in the United States consist of the "No. 12 Alloy" (92% Aluminum, 8% Copper) more or less modified, of course, by the respective mechanical and chemical requirements, while the bulk of the remaining aluminum alloys is made up of other standardized alloys. Bearing metals and other important industrial alloys also have been, or are in the process of being, standardized.

Of still more signal success appear to be the efforts at simplifying and standardizing in the non-ferrous metal working industries, the percentage of reduction of varieties of the different products ranging from 5 to 95 per cent. Thus, of 1114 varieties of brass lavatory and sink traps, simplification and standardization have eliminated 94 per cent, leaving only 72 varieties. Similarly, the reduction in varieties of sterling silver flatware amounted to 67 per cent, that is to say, of 190 varieties of these products only 62 were retained.

A permanent staff located in the Department of Commerce has been organized to co-operate with the manufacturers, distributors, and users, and to bring together the various elements in several industries that share identical problems.

It is self-evident, of course, that in view of the manysidedness of this work and the numerous difficulties to be overcome, progress in simplification and standardization is not as rapid as could be desired, but very much has been accomplished, and there can be no doubt that the united, powerful efforts of all progressive elements directed towards this end will gradually but surely be successful along the whole line.

Apart from the elimination of unnecessary industrial wastes as

such, attention is being paid to the systematic improvement of the quality of the scrap and residues produced. It is obvious that the purer and more homogeneous the scrap and residues, the larger their values and the higher the economic yield obtained in remelting and refining. Careful separation of scrap and residues at the point of production, during transportation, and at the points of destination is an all-important requirement. Particular care is to be exercised to keep deteriorating impurities out of valuable waste products. Thus, iron and aluminum are poison to copper alloys, zinc and arsenic to white metals and lead, tin, and copper to zinc or aluminum scrap, etc.

Large industrial organizations such as Railroads, modern Engineering works, etc., have long since realized the economic value of these precautions, and every possible effort is being made to avoid mixing the different scraps and residues and to prevent their contamination with metallic and non-metallic impurities. Among the non-metallic contaminations of small scrap such as borings, filings, etc., oil and soapwater take a prominent position. The former is now being removed to a large extent by centrifuging, the oil thus reclaimed often paying the costs of the process. Where iron and steel parts are mechanically worked along with non-ferrous metals, all the scrap produced is passed through magnetic separators, while small scrap containing large percentages of non-metallic impurities, such as sweepings, are frequently cleaned by means of air suction or ventilating systems. The separation of white metal and copper alloy turnings by a combined mechanical and thermic process also has been developed to a high state of perfection, although this process really belongs to the sphere of smelter work proper.

Another important factor in the elimination of waste and the reduction of excessive costs is the intelligent mechanical treatment of scrap materials and residues previous to and after transportation to the smelter. Considerable savings may be effected, for instance, by breaking up, or reducing the size of numerous kinds of scrap. Thin-walled scrap such as wire, sheets, bands, etc., should be baled or, if possible, briquetted, while others, such as long turnings, etc., may easily be disintegrated by means of special machinery. Residues containing large quantities of water should be dried wherever cheap sources of waste heat can be made available. The savings in costs of transportation effected by such a reduction of weight and space are appreciable.

Metal scrap and residues may roughly be divided into three groups in accordance with their physical and chemical nature and their source of origin.

1. New metal scrap produced in mechanical working of metals and semi-finished products such as new sheet metal clippings, rolling mill scrap, new metal turnings and filings, etc. Also foundry scrap.

2. Residues produced in metallurgical and chemical processes such as drosses, skimmings, metallurgical slags and ashes, slimes, etc.

3. True "old metals," that is, metallic products which, after having served their purposes, reappear in the metal markets to be remelted and refined, and returned into the metal working industries. These old metals are produced by Railroads, Engineering and Chemical works, Ship-wharfs, etc., and include such materials as old and corroded lead sheeting and piping, antifriction metals, type metal and solder scrap, old copper wire and plates, machine scrap of all description, marine scrap such as ship screws, armatures, plating, marine engine scrap, condenser tubes, etc.

3a. This group includes the many types of domestic scrap such as kitchen utensils made of copper, aluminum, tin and their alloys, tableware, plate, Britannia and pewter scrap, etc.

The second of the above groups represents the most important class of industrial waste products treated by residue smelters and includes the residues and precipitates of the detinning industries, electrolytic precipitates, accumulator ashes and old battery plates, old paint waste, solder and type metal ashes, lead sulphate and other metallic salt wastes, flue dust, sweepings, etc.

A large proportion of metallic scrap, particularly foundry and rolling mill scrap, and large quantities of solder and bearing metal scrap, etc., never reach the open market but is returned to the furnaces from which it came. Where large amounts of scrap or residues are produced by individual manufacturers, these are often sold directly to the smelters, while the rest of the scrap and residues available is handled by the numerous large and small scrap metal dealers scattered all over the large industrial centers of the countries.

The value of the scrap dealer as an independent link between the scrap and residue producer and the smelter has become more or less of a burning question, which is now being solved frequently by direct dealings among producers and smelters, while the scrap dealer, on the other hand, finds it more profitable to install his own little smelt-

ing department in order to meet the competition of the large smelter by melting and smelting some of the less difficult scraps and residues and producing a number of secondary metals and alloys. Those "Back Alley Smelters" often grow quite rapidly—and the result of these adjustments in the scrap dealing and melting trades is that, while numerous of the smaller dealers are gradually being forced out of business, small smelters commence to make their appearance in many sections of the country, cutting down the profits of the large and old established smelters.

There are operating in the United States at this time more than 300 Secondary Smelters, distributed as follows:

Illinois	43	Minnesota	4
Pennsylvania	38	Wisconsin	4
New York	37	Georgia	2
Ohio	33	Nebraska	2
Massachusetts	29	Texas	2
New Jersey	25	Virginia	2
Missouri	22	Alabama	1
Michigan	15	Kansas	1
California	11	Oregon	1
Indiana	11	S. Carolina	1
Connecticut	7	Tennessee	1
Colorado	4	Washington	1
Maryland	4	W. Virginia	1

This process of transformation appears to have developed much more intensively in Germany, where apart from the few large smelters established previous to the War, there are now many medium and small smelting works, while some of the largest and oldest plants such as the Huettnerwerke Tempelhof A. Meyer and Tiede's Eidam were driven out of business.

From a broad economic point of view it appears, indeed, that there is little justification for the existence of a certain group of scrap dealers, comprising some of the large brokers operating between the wholesale dealer and the smelter. It is practically impossible, of course, for the smelter to canvass back yards and small metal working shops for their raw material, and the small scrap collector is required to find and collect the scrap, operating independently or on a commission basis for a large dealer, who grades the raw material and sells it to the smelter or to other, still larger dealers. With a highly developed organization of the scrap dealing and melting in-

dustries, this second dealer should and could be eliminated in many instances, which would reduce the unproductive profits of the trade, representing in most cases the direct cause of the small margin of prices between original and secondary metals and alloys.

The opinion held by many smelter men that scrap and residue dealers tend to more or less dishonest practices by intentionally contaminating good raw materials with cheaper stuff in order to dispose of the latter more profitably, is doubtlessly based on isolated experiences only, and may often be caused by negligence or ignorance on the part of the dealers. Reputable dealers hardly stoop to such shortsighted practices, which can only lead to loss of business. More frequent and consistent use of analytical chemists on the part of small smelters as well as scrap dealers would put a stop to such attempts in any case, apart from placing the scrap dealing and smelting industries on a more efficient basis generally.

More serious is the charge made by producers and consumers alike that the scrap trade as a whole tends to exceed reasonable margins of profit, but this policy—if carried out consistently—is bound to lead to still more intimate co-operation between producers and consumers.

The basic reason for all the peculiarities and traits of the scrap metal and residue industry appears to be a lack of organization, co-operation, and scientific working methods. The relative smallness of the individual dealers and smelters should be no reason for ignoring the modern methods of operation successfully introduced in closely related fields of industry such as the iron and steel industries. Rule-of-thumb methods should be supplanted by scientific and rational operation, and the ancient trade customs still prevailing throughout the non-ferrous scrap and residue dealing trade should be abandoned in favor of modern and efficient business methods.

It is to be hoped that the various societies and organizations now formed, or in the process of formation, will bring about this change within a minimum of time, and that the reactionary spirit of secrecy still considered best policy by most smelters will give way to a free and fertile exchange of ideas and experiences along general lines. Many years of experience of older and more advanced industries have shown that the general advancement of an industry is directly dependent on the degree of co-operation among the individual units, and there appears to be no reason why the scrap metal industry should not realize and apply this principle as well.

CHAPTER I

SMELTING TIN AND WHITE METAL RESIDUES

Since pure tin residues, ashes, slags, dross, etc., are not available in sufficiently large quantities to permit of uninterrupted and efficient production of relatively pure tin, these materials are usually treated together with solder ashes and other lead residues and slags containing considerable percentages of tin, so that in the large majority of smelters the final products obtained are tin-lead alloys of all possible compositions. A discussion of the metallurgical treatment of tin residues cannot, therefore, be limited to the pure materials alone. Indeed, it will be shown that the economical extraction of tin from some residues, such as tin slags, can be effected only if this is bound to another metal.

Tin and white metal may be smelted in reverberatory and blast furnaces, both of which possess certain characteristic advantages depending upon the nature and character of the material treated, although the reverberatory furnace process is now generally considered as representing the most advantageous for the treatment of all types of true tin residues, rich slags, drosses and ashes, particularly if rich in tin. It appears perfectly logical, for this reason, that the blast furnace process is now being replaced by the reverberatory furnace methods of smelting in all parts of the world wherever the material smelted consists of true tin residues or, especially, ores, but conditions in the residue-smelting industries, while similar in principle, vary sufficiently along practical lines to render the strict adherence to ore smelting processes more or less uneconomical.

It is unwise, therefore, to adopt the attitude held by the ore-smelting industry towards the respective virtues of the two processes in smelting tin residues, more or less contaminated as these are with lead and other metallic constituents. Wherever conditions are such that considerable quantities of rich residues can be smelted for the production of tin-lead alloys richer than 45 or 50 per cent, this

is most efficiently accomplished by smelting tin ashes and rich slags in reverberatory furnaces. However, in treating the more common types of tin-lead residues containing 40 to 45 per cent tin or less, the blast furnace has doubtlessly proved to be the most efficient type of smelting appliance. Besides permitting of a more effective removal of the impurities and a cleaner separation of metals from slags, matte, and speiss, blast furnaces give larger yields and require less fuel and labor than reverberatory furnaces.

In considering the qualification of the blast furnace process under varying conditions, the advantages named are accompanied by the following disadvantages:

1. Small-grained, powdered materials, such as a considerable part of the white metal ashes obtainable, cannot be charged into the blast furnace without previous briquetting or slagging. In practical smelting operation this disadvantage is taken care of by giving the residues in question a preliminary reverberatory furnace treatment, subjecting the slagged residues to a final extraction in the blast furnace.

2. The loss of tin by volatilization is somewhat higher in blast furnace smelting, the tin volatilized often reaching 10 per cent of the total amount of tin contained. A large proportion of this metal is regained in form of flue dust collected in the flue channels or in dust-catching devices, of course, but the net loss of tin is still higher than that suffered in reverberatory furnace smelting unless modern dust catching devices, such as the improved types of bag filters or the Cottrell system of condensation, are installed. It is also possible to effect a reduction of the percentage of tin lost by volatilization by increasing the height of the furnace shaft, although beyond a certain maximum height the melting capacity of the furnace is appreciably diminished.

3. As a rule, the tin or tin alloys produced in blast furnaces contain appreciably larger percentages of iron than the respective products resulting from the reverberatory furnace process. It should not be too difficult, however, to make up the charges in such a way as to conduct the bulk of the iron present in the charge constituents into the slag or, eventually, into the matte and the speiss.

4. In many instances it is found that exclusive use of the ordinary grades of blast furnace coke causes a decided increase of brittleness of the tin produced. It is absolutely necessary in such cases to employ a certain percentage of high grade charcoal. In spite of its physical disadvantages, charcoal, on account of its high degree of

purity, gives best results, although the improvements of the mechanical properties of the tin produced is accompanied by a correspondingly serious deterioration of blast furnace efficiency if more than half of the coke is replaced by charcoal, particularly in comparatively large and high blast furnaces.

While it is possible, therefore, to make use of the various valuable advantages of blast furnaces by eliminating their most important disadvantages, conditions will arise where reverberatory furnace treatment of tin residues offers the only acceptable solution.

The Reverberatory Furnace Process.—The size of reverberatory furnaces depends in the first place upon the amount of material handled by the smelter. The larger the furnace the higher the degree of efficiency attained, the less the proportional amount of fuel and reduction material required, and the smaller the percentage of metal lost by gasification and slagging. While the hearths of very large ore reverberatory furnaces, as, for instance, those of the Straits Trading Company, measure above 250 square feet, decidedly smaller furnaces are employed for smelting tin and white metal residues. As a rule, the hearths of these furnaces are 8 to 11 feet long and 6 to 8 feet wide. The inclination of the hearth towards the tap amounts to about 1 inch per 3 feet of hearth length, its concavity to about 1 inch per foot. Figures 1 and 2 show the construction of a typical reverberatory furnace suitable for the treatment of the usual type of white metal and tin residues.

While the general construction of tin and white metal reverberatory furnaces does not differ from that of any other furnaces of this type, attention is called to the fact that tin and its alloys possess a much stronger penetrative action towards the brickwork of the furnace than most of the other common metals, or metallic alloys, and it becomes necessary, therefore, to consider this property in constructing the bottom of the furnaces. As a rule, the bottom is composed of four layers of bricks, the two lower layers consisting of ordinary fire-clay bricks laid flat. The third layer consists of good grade fire-clay bricks (about 32 to 33 Seger cone) laid on edge, while the top layer is built of high grade bricks (34 Seger cone) standing on end. The dimensions of the bricks should be such as to eliminate the necessity of cutting or chipping.

The bottom rests upon cast iron plates which repose upon heavy girders stretched across a cellar or vault. Attention is called to the arrangement indicated in Figure 1. The bottom plate is slightly

declined towards the firebridge where it rests upon a trough commonly made up of a large size U-iron. The white metal penetrating the hearth is thus collected at one point and may be recharged immediately.

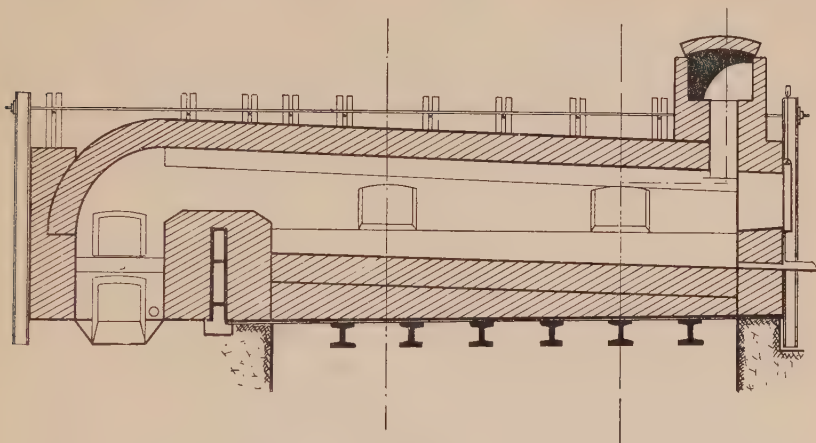


FIG. 1.

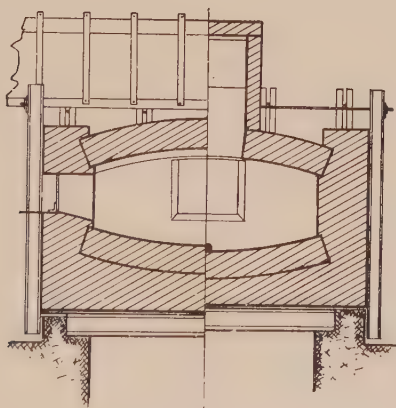


FIG. 2.

FIGS. 1 AND 2.—REVERBERATORY FURNACE FOR WHITE METAL AND TIN RESIDUES.

This type of construction is advisable only, however, if the cooling space of the firebridge is air-cooled, that is to say, if a jet of cold air, produced by a small ventilator, is directed into the cooling section from one side of the furnace. Experience has shown that this

precaution will prevent excessive leaking of tin as well as of all white metals through the firebridge. Water cooling is not required for this purpose. (For detailed discussion of this subject the reader is referred to the special chapter on Reverberatory Furnaces, page 255.)

The walls of tin and white metal reverberatory furnaces are usually made 18 inches thick. The smaller types of furnaces, such as are commonly employed in residue smelters, are provided with two working doors, both to be near the flue opening.

Where space is no object, the hearth of residue smelting white metal reverberatories should be made as flat as possible, in order to secure a large surface of charge and to facilitate slagging. The same is true of straight liquation furnaces, or where smelting and liquating is to be carried out in the same unit. If, on the other hand, one reverberatory is to take care of all processes incident to white metal smelting and refining, as is often necessary in small plants, the hearth should be made somewhat deeper, the maximum depth ranging from 12 to 15 inches.

Treatment of Metallic Drosses and Skimmings.—Before treating these and similar residues consisting more or less of metallic constituents in reverberatory furnaces, they are usually subjected to a preliminary treatment in melting pots or small liquating-reverberatory furnaces in order to extract as much metal as possible. If they contain considerable quantities of sulphur, arsenic, iron, copper, or antimony, they are subjected to a combined liquating and roasting treatment, raising the heat very gradually until a hard and powdery residue remains, which is then added to the other residues.

This primitive liquating treatment is now frequently replaced by the modern segregation process adapted to larger quantities. Four or five tons of this semi-metallic material are collected and charged into a reverberatory furnace in lots of about 500 pounds each until the hearth of the furnace is half filled with metal. The ashes collected on top of the metallic bath are drawn off and fresh material charged until the furnace is almost filled with metal. After removing all of the ashes, the metal is heated to a temperature of about 1450° Fahr. and the arsenic removed by washing the metal with thin iron scrap, such as wire, sheets, etc. In the meanwhile, the temperature of the metal has gradually been raised to 1550°–1600° Fahr., and it is then puddled for about 10 minutes in order to remove all of the zinc and part of the sulphur present. It is not necessary

to remove all traces of sulphur at this stage of the process, since the metal will be entirely desulphurized at the final steaming. Puddling completed, the metallic bath is cooled down as rapidly as possible, firing being stopped and all working doors opened. The metal is tapped at a temperature of about 850° Fahr. The treatment of the residue is described on page 127.

Quite frequently, white metal drosses and other materials contain large percentages of metallic particles which may often be removed—in part, at least—by screening. If the metallic constituents are present in form of powder or very small particles, and the quantities of this material contained in the ashes are sufficiently large to pay for additional efforts, the ashes may be subjected to a washing treatment, the poor ashes being run into tanks or pits and the water drained off. The metallic residues are dried and charged into melting pots, together with a little coal dust, and melted. The treatment of the white metal alloys obtained will be described in another chapter. (Page 113.)

Treatment of Oxidized Metallurgical and Chemical Tin Residues.

—The most important sources of these residues are the ore metal smelters, the various industries producing tin articles, and chemical works, such as paint works, dye works, galvanic tin-plating and detinning works, etc. While metallurgical residues, irrespective of composition and source, may be subjected to the smelting treatment without preliminary treatment, excepting, perhaps, the separation of the bulk of the metallic constituents present, tin residues obtained from chemical industries may often require preliminary treatments, such as leaching, etc., to remove excessive acid contents, sulphur or sulphides, etc.

This is especially necessary where the tin is present in form of chlorides, or where hydrochloric acid or volatile chlorides are contained in the residues, which are bound to cause an excessive loss of tin by volatilization. The leaching solution obtained, which always contains considerable percentages of tin compounds, is treated with milk of lime, and the pasty precipitate added to the reverberatory charges.

Acid residues produced in chemical works are neutralized with lime or soda ash, residues containing sulphides are subjected to a preliminary roasting treatment. Chemical waste solutions containing tin are decomposed hydrolytically, or the tin is precipitated by addition of milk of lime, while the resulting paste is either added to the

reverberatory charges, or dried, calcined, and finish treated like tin oxide.

Charge Mixtures.—Since, as a rule, residual tin ashes contain only the oxides of tin and lead as well as those of metallic impurities—apart from certain small amounts of metal—slag forming materials are not always added. Soda ash should not be added in excess. Although producing a somewhat more liquid slag, this serves no practical purpose whatever, but exhibits a strongly corrosive influence on the refractory linings of walls and bottom of the furnace.

It will be found, however, that in spite of theoretical considerations, slag-forming materials, including soda-ash, are practically always added in most residue smelters. This practice is claimed to hasten the melting process and to prevent excessive volatilization of metal.

Conditions are considerably more complicated where the residues contain appreciable quantities of iron, iron oxides, or silica. Metallic iron is removed mechanically by passing the residues over magnetic separators, while the presence of iron oxide, lime, or silica require the addition of other slag forming materials to produce a satisfactory slag.

In making up a suitable slag mixture for this purpose the following factors must be considered:

1. The total amount of slag formed must be as small as possible, since even the most satisfactory slag will take up considerable percentages of tin.
2. Slags rich in iron are comparatively poor in tin, but will cause the introduction of appreciable quantities of iron into the tin.
3. Slags rich in silica tend to take up large percentages of tin in form of tin silicates.
4. If in replacing part of the iron to make up a certain type of silicate too much lime is added, lime stannates are formed, from which the tin is removed only with difficulty. High-lime slags are also unfavorable on account of their corrosive action on the refractory linings of the furnace, resembling that of soda ash.

Thus, it appears that in treating residues containing iron oxide as chief impurity, silicious material alone is added, while in the case of strongly silicious residues iron oxide and a little lime is added, the amount of the latter not exceeding 10 or 15 per cent of the iron oxide entering the slag. Since in the treatment of residues the chief requirement should always be the production of as pure a tin or white

metal as possible, and since all slags obtained from this process must be subjected to a final smelting treatment, it is advisable to make up a comparatively silicious slag. The amount of lime, alumina, and magnesia present in the residues is calculated as basic material against the silica.

The above pertains to pure and semi-pure tin ashes. For the common run of white metal ashes, or where the melting points of the slags must be maintained as low as possible to conform with limited furnace temperatures, numerous other complex slag compositions are produced. It is practically impossible to give slag compositions suited to all general purposes, particularly where the composition of the raw materials changes with every other charge, and the best practice in this case appears to be to select one basic slag mixture containing about 45 per cent iron oxide, 25 per cent sand, 10 per cent lime and 10 to 20 per cent fluorspar, modifying this composition to suit the varying requirements. If soda ash is to be added at all, this should be left out of the original slag mixture and added in small portions later, that is to say, as soon as enough slag has formed to indicate its fluidity and general properties. The author has found that in contrast to accepted European practice most American smelters enforce the fluidity of their slags by the addition of a safe excess of soda ash. While the presence of considerable percentages of soda ash is bound to produce fluid slags, smelting costs are increased and the life of furnace refractories shortened in proportion to the percentages of this alkali present.

The treatment of the rich slags produced will be considered separately.

The tin residues are mixed with the requisite amounts of slag forming materials and with 3 to 5 per cent of finely powdered anthracite, and thoroughly mixed. The mixture is moistened to prevent excessive dusting during charging.

The amount of material charged depends upon the size of the furnace, i.e., the hearth area, the thickness of layer ranging from 5 to 8 inches. The charge is spread out evenly over the hearth, excepting a small section of the hearth around the tap hole, which must be kept free to prevent the clogging up of the tap by a hard metal oxide-slag mixture. All working doors are then closed and luted, and the charge is subjected to an even heat of not more than about 2000° Fahr. for about one to two hours. The working door located in the narrow front side of the furnace, directly beneath the flue-intake,

is then opened, the charge rabbled thoroughly, again spread out, and the door closed and luted. The furnace temperature is then increased to the limit, the gases of combustion remaining distinctly reducing at all times. In rabbling, care must be exercised not to stir up the metal more than can be helped, while immediately previous to rabbling two or three shovels full of ground anthracite or coke are spread over the charge, to make up for the carbon oxidized throughout the process. After several hours, the charge has become more or less liquid, and the emission of the typical thin flames, indicating the combustion of carbon monoxide gas, begins to cease. As soon as all the material charged has become liquid, the furnace is definitely closed and the charge left at high heat for about one hour. The end of the smelting process is determined by dipping a cold iron rod into the slag and examining the adhering skin of cold slag for metallic globules.

Tapping the Reverberatory Furnace.—If the slag test proves the slag free from metallic ingredients, the furnace is tapped. A pointed iron rod is driven through the clay plug at its lowest point. As soon as all metal has drained off and slag begins to make its appearance, the tap hole is opened entirely. Towards the end of the slag flow the working door above, or nearest to, the tap hole is opened and all the metal and slag collected near the tap is pushed through the hole. The remainder of the viscous slag and the other residues left on the hearth and near the firing bridge is collected near the firing bridge and a new charge of residues, or rich slags, deposited on top of the old slag in order to prevent the considerable percentages of metallic tin, etc., still contained in this slag from vaporizing.

The treatment of straight white metal ashes in reverberatory furnaces does not differ in principle from that of pure tin materials. The most important practical difference appears to be made in the treatment of the slags, which are not, as a rule, retained in the furnace to be subjected to a second or third smelting process. Where the reverberatory furnace employed for this purpose is supplied with a slit tap, the slag is drawn off into slag cars which are removed to the dump and emptied after cooling off completely. The white metal cone collected on the bottom of the pot is recovered and the rest of the slag is collected until enough has accumulated to fill a furnace. The white metal contents, metallic as well as slagged, are then precipitated by mixing the fused slag, with about 5 per cent

of coal and 3 per cent of lime, and heating to about 2000° Fahr. for 2 or 3 hours. The clean slag may then be disposed of, although a number of smelters prefer to add the crushed slag in small quantities to regular charges, where it serves to hasten the softening process. Thin-walled iron scrap is often used together with lime to precipitate white metal from rich slag.

Where reverberatory furnaces are operated with bottom tap, the slag is either pulled out before tapping, or it is tapped after the metal.

Smelting Pure Oxides.—It has been pointed out before that if, apart from a certain quantity of metallic particles, tin ashes contain the oxides of metals only, slag-forming materials being absent, the formation of a slag is not required to produce satisfactory results. The ashes are mixed with about 5 to 8 per cent of finely ground anthracite, moistened, and charged, the depth of the charge layer in this case averaging 4 to 6 inches only. The operation of the smelting process does not materially differ from the treatment of impure ashes, although the individual periods as well as the total length of the process may be shortened to some extent. Instead of leaving the charge remain at rest for up to two hours before commencing rabbling, only half an hour or, at most, one hour is allowed for the considerably thinner layer of ashes to arrive at the heat of the process. The various rabbling periods also follow each other in shorter order, best results being obtained if the charge is rabbled every 30 minutes.

While it is the practice of some smelters to leave the tap holes open at all times throughout the process to permit the freshly formed metal to leave the furnace immediately, thus preventing oxidation and volatilization, this is not to be recommended, since, on account of the cold air which is constantly drawn through the tap hole into the furnace, the tin passing through in thin rivulets will tend to freeze up the hole, causing no end of trouble. Besides, it is hardly consistent with the principle of attaining highest temperatures, if a constant stream of cold air is permitted to enter the furnace.

With the average type of tin ashes, a charge of about 4000 pounds of material may be worked through within about three to four hours. The residues remaining in the furnace after tapping are not removed, the fresh ashes being charged on top of them.

Unlike the treatment of tin ores or tin ashes containing large percentages of slag forming materials, absolutely no trouble is occa-

sioned in smelting tin ashes of ordinary purity if the temperatures are maintained sufficiently high, and the furnace atmospheres are kept strongly reducing. If, for some reason, the resulting slag is very tough, a little fluorspar may be added to soften it and to permit the grains of metal to settle out.

If the semi-melted residue remaining on top of the metal at the end of the process is found to contain a large amount of metallic pellets, it may be mixed with a few shovels full of unslaked lime, the mixture rabbled for a few minutes—care being taken not to disturb the bath of metal too much—and exposed to the full heat of the furnace about 30 minutes. By this treatment, a large proportion of the mechanically suspended metal is liberated and returned to the metallic bath. Care must be exercised, however, not to add too large a quantity of lime, since this will destroy the slaggy nature of the residue which assumes a dry, powdery consistence and becomes unsuitable for the final blast furnace treatment.

Mention should here be made of the so-called “tin-ashes” produced in refining lead which, depending upon the method of oxidation applied may contain from 5 to 25 per cent of tin. If this product is treated with the object of extracting the tin with the lead, comparatively high temperatures and strongly reducing conditions must be maintained, the product obtained forming quite a good base alloy for type metals, etc. Very different results are attained if the smelting process is carried out at comparatively low temperatures, that is, about 1650° to 1700° Fahr., and the furnace atmosphere maintained as nearly neutral as possible. This prevents the bulk of the tin oxide present from being reduced, so that while the lead produced is comparatively pure (99 to 99.5 per cent), the tin is concentrated into the residues, which may then be treated together with high percentage tin ashes.

The tin produced in melting pure tin ashes is rarely pure, the quantity and quality of the impurities contained depending upon the composition of the material smelted as well as on the furnace conditions. Since many so-called tin ashes are really mixtures of tin and lead oxides, the products are very often straight tin-lead alloys. The treatment of these alloy products will form the subject of another chapter.

Smelting Tin Slags in Reverberatory Furnaces.—Tin slags are logically subdivided into rich and poor slags. Rich slags, which are obtained in smelting tin ores and ashes, always contain considerable

quantities of unreduced oxides and slagged tin in form of tin silicate, calcium stannate, sodium stannate, etc., chiefly, however, metallic tin in globules and small particles which remained suspended in the slag, or were washed out on tapping the slag. The tin contents of this material vary considerably, even with subsequent charges, and are usually recovered in the reverberatory furnace.

Mechanical separation of the metallic tin from rich slag by grinding the material and washing or sifting out the metallic particles is uneconomical, even if this treatment is only extended to the larger pieces of metal present. The relatively large amounts of unreduced tin oxide and compounds present, which cannot be removed along with the metal, require a smelting treatment in any case, and since the product obtained is not much more impure than the metallic tin suspended in the slag, there appears to be no reason for an expensive preliminary treatment.

For reverberatory smelting the slags are crushed to about walnut-size, mixed with 5 to 10 per cent of reducing coal and smelted at the full heat of the furnace, comparatively pure metal and "poor" slag resulting.

Semi-metallic residues, such as dross, skimmings, etc., may be smelted along with the slag, wherever the nature of these residues, that is, the quantity and quality of the metal contained, does not necessitate separate treatment. It is also possible, of course, to add rich slag to tin ashes, where the production or presence of a certain quantity of slag is desired.

The poor slag obtained from the rich-slag treatment cannot economically be smelted in the reverberatory furnace, sufficiently clean slags being obtained only by running the material through the blast furnace, alone, or together with other tin-residues.

The Tin Blast Furnace Process.—While the old types of tin blast furnaces represented heavy stone and brick constructions of square, semi-circular, and trapezoid cross section, supplied with one or two tuyères, and frequently devoid of water jackets, modern constructions, if purchased from manufacturers, consist of easily transportable steel mantles lined with a comparatively thin wall of high grade refractory bricks, and supplied with four to eight tuyères of varying cross-section. Water jackets are not always used with tin blast furnaces. These light furnaces are rarely used for smelting tin ores but give very good results with tin ashes of all kinds, as well as with the various types of tin slags. Since tin blast furnaces

permit of a high degree of separation of copper, antimony, and tungsten, which are largely removed by volatilization and slagging, they are generally believed to be greatly preferable to reverberatory furnaces in smelting tin residues high in impurities of this class. Where comparatively rich tin ashes, low in lead contents, are smelted with a view to removing most of the lead present, this may also be achieved by correct application of the blast furnace process.

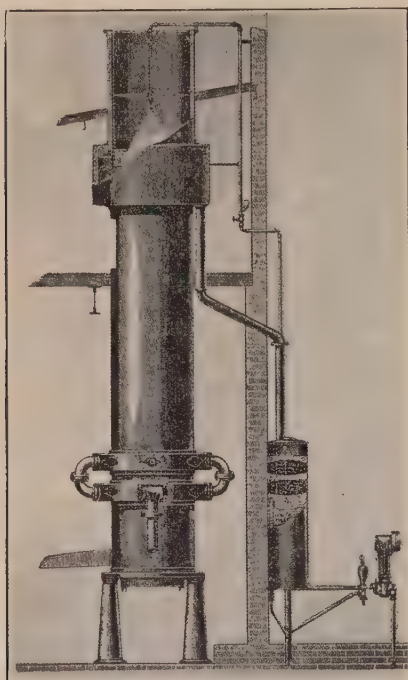


FIG. 3.

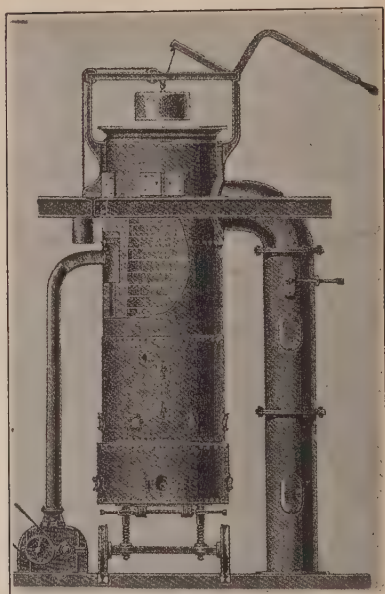


FIG. 4.

FIGS. 3 AND 4.—EUROPEAN BLAST FURNACE FOR TIN RESIDUES.

Figures 3 and 4 show two types of blast furnaces used in many European countries which are eminently suitable to the treatment of tin ashes and other tin residues.

Figure 3 shows the application of a water spray used to decrease the amount of tin primarily lost by volatilization. While this arrangement is said to be giving good results in some instances, its use has been discontinued in most smelters, primarily because its basically correct principles can be evaluated only if a number of

factors, more or less modified by various conditions, are continually considered and reconsidered to apply to the ever-changing conditions of blast furnace operations. It is quite obvious, however, that with gradual perfection of this arrangement it may prove to become a very valuable device for the prevention of excessive volatilization losses in tin blast furnace operation.

The tin blast furnace shown in Figure 4 is characterized by its comparative shortness and the side outlet for the blast furnace gases and vapors generated. While this type of furnace may be of value in smelting tin slags, where the decreased height of the shaft tends to counteract the reduction of the iron oxide contents of the slag, thus preventing excessive contamination of the tin with iron, it does not represent an ideal smelting device for tin ashes and similar residues rich in metallic contents; sufficiently high extraction of these materials requires the maintenance of a comparatively high charge column.

The side-outlet for the blast furnace gases and vapors also appears to be unsuitable for tin blast furnace operation. Being drawn off at the side of the furnace, the gases will not pass up the center of the column, where they are able to effect the chemical reactions necessary, but are practically forced to ascend along the walls of the shaft. While, theoretically, this may be avoided by charging the materials so as to concentrate the fines around the sides of the charge column, thus offering the gases a path of least resistance through the coarse material in the centre, this method of charging is not only tedious, causing the furnace crews to disregard it wherever possible, but does not insure sufficiently perfect separation of fines and coarse material further down the shaft.

Another factor of importance to be considered in this connection is the much greater loss of tin by volatilization if the vapors are drawn off at the side of the furnace. If the hot vapors are able to ascend through the entire charge column, they are permitted to cool off considerably while passing through the upper cold layers of the charge, while further condensation is effected during the passage of the vapors through the open hood above the shaft. This is not possible, however, where the gases and vapors are drawn off comparatively far below the top of the charge column.

The above disadvantages are shared by the side outlets of other white metal blast furnaces also, of course, but the advantages claimed for this type of construction are not overshadowed as seriously by

the disadvantages enumerated where the monetary value of the metals is as far below that of tin as in the case of lead or antimony, etc.

Figures 5 and 6 show a tin blast furnace built by the author for a number of German, Dutch and Norwegian smelters which has given good results in smelting rich and poor tin residues of all kinds.

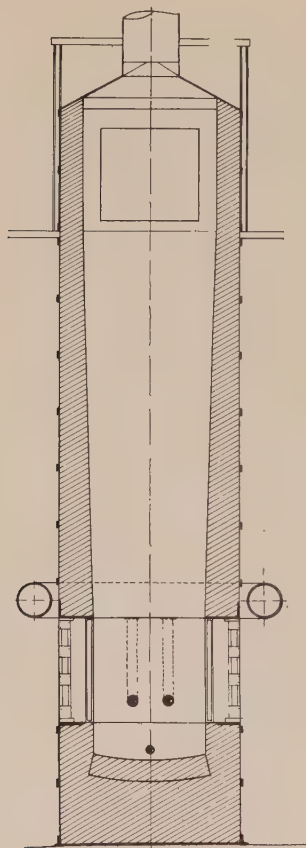


FIG. 5.

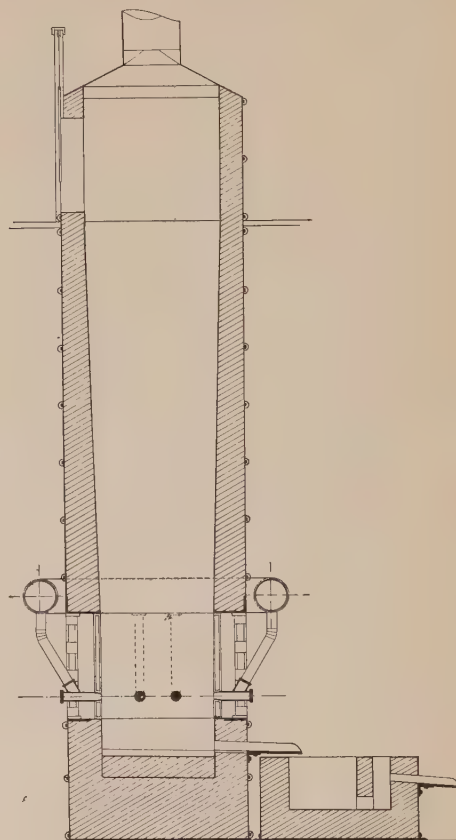


FIG. 6.

FIGS. 5 AND 6.—TIN BLAST FURNACE.

While the shaft is a little too high for tin-slag smelting, the charge column may be lowered at will by keeping the surface of the column as far below the charging floor as is necessary to obtain best results.

The furnace is supplied with water jackets on two opposite sides, each of them holding two tuyères. The distance between the tuyères,

that is, the width of the shaft between the water jackets, is 35 inches. Slag and metal are not tapped periodically, but leave the furnace together through an open tap as soon as formed, flowing into the forehearth shown.

Where the tin produced contains a comparatively large percentage of iron, the open tap should not be employed, since the tin-iron alloys formed possess a rather high melting point and tend to chill easily. It is necessary in this case, therefore, to operate with interior crucibles where the metal remains under the influence of the heat of the furnace until tapped. However, since in general residue-smelting practice true tin residues are relatively poor in tin, and since in most cases residues rich in lead make up the bulk of the blast furnace charges, lead-tin alloys (rich solder alloys) are usually produced, when blast furnaces operating with open taps invariably give best and most economical results.

Smelting Operations.—In smelting residues rich in tin, no attempts should be made to obtain slags poor in tin at the first operation, since the slags produced will always turn out to be too rich in metal to be discarded and must therefore be subjected to a second or, even, third smelting. The purpose of the initial smelting treatment of the residues is best served if main attention is being paid to the production of large quantities of as pure tin or tin-alloys as possible. It is also good policy not to adjust this smelting process to the treatment of certain single raw materials, but to the production of certain alloys rich in tin useful as base alloys in the manufacture of technical alloys, such as solders, bearing metals and similar compositions.

In making up the charge mixtures, attention should be paid to the fact that, while the majority of tin residues, including the ashes, scums, dross, segregation and liquation residues, etc., may be treated together, tin slags are most economically smelted separately, unless these are used as slag forming components, when the addition of certain proportions of the poorer varieties to the residue charge mixtures may be justified. The treatment of tin slags will be discussed separately.

The raw materials suitable for blast furnace smelting are mixed with the requisite amounts of coke, lime, iron oxide, and other slag-forming materials, and with sufficient quantities of thin-walled iron scrap to combine with the harmful ingredients of the charges, i.e., arsenic and sulphur, and to assist in the reduction of metallic oxides.

Tin-plate scrap offers the best iron material for this purpose. As a rule, a small amount of a ground up mixture of equal parts of soda ash and solder ash is also added. The presence of much powdered or small grained raw materials in the charges must under all circumstances be avoided, since relatively small percentages of this will appreciably lower the melting efficiency of the process and cause a correspondingly large increase of loss of tin by dusting and volatilization.

In order to keep smelting efficiency at a maximum and to reduce the loss of tin by volatilization to reasonable figures, it is necessary to pay close attention to the exact proportion of coke added to the charge. As a rule, 8.5 to 9 per cent of coke will be found to suffice. If the quantities of coke added exceed the required proportion, large amounts of hot carbon monoxide gases are forced up through the charge, bursting out in flames at the level of the charging floor, and the heavy white fumes evolved are sufficiently clear evidence of the quantities of tin and other metals burned.

The effects of a small excess of coke above the usual 9 per cent may prove a distinct advantage in that the smelting capacity of the blast furnace is increased in proportion. However, beyond a certain percentage of coke, approximately 11 per cent, the smelting capacity is actually decreased in proportion to the additional time required to gasify the excess fuel. In addition to the excessive quantities of carbon monoxide formed, the surplus of coke may cause the fire to rise towards the top of the charge column.

Similar difficulties are caused by the addition of insufficient percentages of coke to the charge. Since the quantity of coke passing down to the tuyère region does not suffice to satisfy the normal reduction processes involved, the zone of reduction, or reaction, is carried higher and higher up the shaft of the furnace, the hottest section of the smelting column being transferred from the tuyère section, where it is supposed to be, to some part of the shaft above this section, preventing the reduction of a considerable portion of the tin contents of the charge which are vaporized instead.

A natural consequence of the change of location of the zone of reduction is the chilling of the tuyère section by the cold blast, cooling off the slag, and retarding the entire operation of the blast furnace in a steadily increasing degree, so that if the amount of coke added is not quickly increased to the exact percentage required, the furnace will be frozen within a few hours.

In considering the main symptoms of excessive or insufficient additions of fuel to blast furnace charges, that is, the raising of the zone of reduction above the tuyère section and the appearance of top fire at the surface of the charge column, attention should be paid to the fact that similar difficulties may also arise where the percentage of coke carried by the charge is well within the range calculated to give best results. For instance, by working with too small individual charges, where the layers of coke interposed between the layers of residues and fluxes follow too closely upon each other, the fire, driven on, as it is, by the blast, gradually rises to the top, vaporizing large quantities of metal and leaving the tuyère section cold and unresponsive to normal treatment.

While it is not very difficult to locate the specific sources of trouble in each and every individual case, the cures applied are often more or less unreasonable, or even dangerous. It should not be attempted in the first place to eliminate the trouble developed by merely removing the causes, that is, by increasing or decreasing the percentages of coke added, or by adapting the size of each charge to the cross section of the furnace and the nature of the residues treated. The reduction of blast pressure, which is occasionally recommended as a remedy against top fire, will often cause more harm than good, and all of these methods, if applied hastily or out of conjunction with other steps tend frequently to increase the difficulties encountered by reducing the temperature of the tuyère section still further.

Changing the coke charges to correspondingly measured charges of charcoal, or mixing the two fuels, is not to be recommended in residue smelting, and the addition of charcoal, alone or together with coke, will tend to give good results only in smelting rich or poor slags. Pouring or sprinkling water over the surface of the charge is another common "trick," which never will be able to cause the blast furnace to function correctly, since after the rapid evaporation of the water added, the top fire will reappear almost immediately.

The only correct method of curing top fire is to allow the charge column to sink down a little and adding two or three straight slag charges—containing, perhaps, 6 to 7 per cent of coke—thereby forcing the fire down sufficiently far to gradually return to its normal location.

Tin Blast Furnace Slags.—It is self-evident that satisfactory technical and economical results can only be obtained if the slags produced are closely adapted to prevailing circumstances.

Apart from the influence of the metallic raw materials and their constituents on the composition of the slags, this is determined in the first place by the type of process to be carried out and by the composition, that is to say, the metallic contents of the final slags to be produced. It has already been stated that in smelting metallic residues, irrespective of composition, it is not good policy to run the process so as to obtain poor tin slags, but that the residue smelting process should be carried out in two stages, the first being designed to recover the bulk of the values in the residues without paying attention to the metallic contents of the slags produced, while the final smelting operation is to recover the lead and tin contents from the rich slags.

In following this two-stage method it is possible, therefore, to pay particular attention to the production of as pure a metal or alloy as possible, the chief impurity carried into the metal being the iron components of the slag, and the slag produced during the first stage of the smelting process should for this reason be as poor in iron as it is compatible with sufficiently rapid smelting. The type, or types, of slag conforming with this requirement are those ranging from the acid singulo-silicates up to the basic bi-silicates, or, in other words, basic or acid sesqui-silicates, depending upon the prevailing conditions. The sesqui-silicates correspond to the iron oxide-silica compound $4\text{FeO} \cdot 3\text{SiO}_2$ and are comparatively easily fusible, although for a number of practical reasons, outlined on pages 162–163 a certain percentage of lime, not exceeding 10 to 15 per cent of the iron contents, is always substituted for iron oxide. It should also be remembered that the tin oxides dissolved in the slags, which in the case of the silicious slags indicated amount to 5 to 12 per cent tin, will also require a certain quantity of silica, although as a rule, this is not included in the slag computations.

The second stage of the process designed to recover the bulk of the metallic contents of the foul slags produced in the first stage requires a slag comparatively poor in silica and rich in basic oxides. A slightly acid singulo-silicate, corresponding to an iron oxide-silica content of about $2\text{FeO} \cdot \text{SiO}_2$ is usually employed for this purpose, the percentages of lime added ranging from 10 to 15 per cent. It is obvious that the recovered metals or alloys contain comparatively large amounts of iron, but the expenses involved in a subsequent refining process are more than made up by the correspondingly smaller quantities of valuable metal left in the poor slags. Waste slags

should not contain more than 1.5 or, at most, 2.0 per cent of tin. If more tin is carried off, the slag should be smelted a third time, and the efficiency of the smelting operations is not exactly increased by this repeated resmelting, even if the second slag is smelted together with poor tin residues.

The Blast Furnace Smelting of Rich Tin and Tin Alloy Residues.

—While very rich and pure tin residues are usually smelted in reverberatory furnaces which alone permit of the production of comparatively pure products or tin-lead alloys with more than 60 per cent tin, blast furnace smelting is most efficient with charge mixtures composed in such a way as to give a lead-tin alloy containing 40 to 50 per cent of tin. Loss of the valuable metals by volatilization is comparatively small, while in spite of rather rapid operation the slags produced are not excessively rich in tin.

The charge is usually made up of solder ashes, tin ashes, lead ashes, dry drosses obtained in the manufacture of solder and similar alloys, rich slags in suitable amounts to effect fluxing of the charges, a certain amount of iron—preferably tinplate scrap—to supply the metallic iron needed for perfect reduction of the oxides and to take care of the sulphur and arsenic present in the charges, suitable tin ores containing an excess of iron oxide or silica, according to circumstances, and other slagging materials. The fuel consists of coarse coke.

In order to reduce the melting temperatures of the slag and to increase its fluidity, thus causing saving of fuel, decrease of loss of metal by volatilization, and the production of poorer slags, a little soda ash, ground in with solder ash, is usually added to the charge.

The success of the blast furnace treatment is influenced to a high degree by the amount as well as the size of the coke added. The deteriorating action of too large and too small coke charges are generally known, and has been described above. The influence of the size of the coke on the success of the process is less generally realized. It is clear that in the interest of rapid work the coke used in smelting rich tin residues must be much coarser than that used in slag cleaning, where in the interest of most complete reduction fuel and tin bearing material must remain in contact with each other for as long a time as possible and where reducing conditions must be much stronger pronounced. If, on the other hand, the coke used is too coarse, especially in connection with coarse grained charge materials,

the furnace operates too rapidly; there is too much oxidation of iron and tin, and the slags produced are too rich in tin.

The metal or metallic alloy obtained should consist of 40 to 50 per cent of tin and 60 to 50 per cent lead, the antimony contents varying from 1 to 3 per cent, depending upon the amount of this element present in the raw materials and the conditions of the process. The other products are:

Solder Speise, chiefly composed of iron and tin, and containing varying percentages of arsenic and antimony, depending upon the amounts of these metals present in the raw materials and on the smelting conditions.

Rich blast furnace slags containing from 5 to 12 per cent of tin.

Fumes and dust collected in the flue pipes and channels. Speise and fumes contain from 30 to 40 per cent tin and are permitted to accumulate until sufficiently large quantities have been collected to allow of separate treatment.

Since in smelting this material the main object is to remove the excessive iron contents of the speise, the charge must be made up so as to exert a pronounced oxidizing influence on this element. Very suitable oxidizing agents are calcined tin-fumes and heavy lead oxides, while the other materials added to the charge are: Solder speise, rich slags (solder and tin-ore slags), tin plate scrap, and coarse coke.

Antimonial and coppery material should be kept out of the charges as far as possible. Coppery material particularly tends strongly to increase the amount of dross formed on draining the product of the blast furnace process. Attention should be paid to the fact that the fumes obtained from the smelting treatment of tin residues are often contaminated with antimony, so that the composition of these raw materials should be closely controlled.

In view of the strongly oxidizing nature of the process, it is obvious that the slags cannot be made sufficiently poor in tin, the average tin contents ranging from 4 to 6 per cent, while the iron oxide contents are relatively high.

The metallic alloys obtained from speise and fume smelting contain about 20 to 25 per cent tin. The solder speise produced is much poorer than the original speise contained in the charge, averaging about 7 to 11 per cent of tin.

The Smelting of Rich Tin Slags.—Rich, or foul, slags may be de-tinned by two blast furnace methods:

(a) Smelting with lead residues for the production of lead-tin alloys containing from 5 to 25 per cent tin.

(b) Smelting with coke and iron oxide, recovering the tin as an iron-tin alloy containing from 25 to 40 per cent tin.

While the second method is used in some English and European smelters, the first process is applied in the vast majority of instances, the only important advantages of the second method, the production of alloys richer in tin, and of much poorer slags, averaging 0.50 to 0.75 per cent, being accompanied by a number of serious disadvantages.

The most serious disadvantages of this process are the necessity of remelting the tin-iron alloy in order to eliminate the iron, and the low degree of fluidity of the tin-iron alloys produced.

In order to decrease as far as possible the solubility of tin or tin oxide in the slags, these must be rich in iron, the amount of iron contained in poor tin slags averaging 45 to 50 per cent iron oxide (FeO), but blast furnace conditions must be such as to carry all the iron contents of the charges into the slag, and into the matte and speise. The necessity of maintaining a maximum amount of iron oxide in the charge column is obvious. The higher the silicon contents of the slag, the more difficult is the reduction of the tin oxide by carbon or, even, iron. While carbon alone is able to reduce the oxides of tin, it does not separate the tin from tin silicate, which is decomposed only by metallic oxides possessing a higher affinity for silica than stannous oxide. Of these oxides iron oxide is the most practical and efficient. Besides, tin slags always contain a certain proportion of metallic tin present in form of shots or globules which are held in suspension by the viscous acid slags. The higher the iron oxide contents of the slag, however, the more pronounced its fluidity and the more complete the separation of the metallic contents of the slag.

The direct influence of metallic iron on the precipitation of tin is still a matter of considerable divergence of opinion. There can be no doubt, however, that while a certain direct action cannot be denied, this is comparatively insignificant under ordinary blast furnace conditions. Where the tin slag smelting process is designed to furnish the tin as tin-iron alloy, the action of metallic iron is almost exclusively secondary in nature, collecting as it does the reduced tin and carrying it down to the well of the blast furnace.

Where the tin contents of the charges are recovered in form of

lead alloys, the direct action of metallic iron is directed towards combining with arsenic, sulphur, and antimony to form matte and speise, and to reduce a certain percentage of the highly oxidized lead contained in the charges.

The Production of Tin-Lead Alloys from Rich Tin Slags.—Since, as has been stated above, tin slags are most efficiently smelted with the aim of concentrating the tin contents in a lead alloy, this process alone will here be considered in detail. The possibilities of this process are limited by two considerations; while on one side it is the aim of the operator to produce an alloy as rich in tin as possible, the amount of tin remaining in the slag is almost directly proportional to the percentage of tin contained in the alloy. It is well possible, however, to work towards an 18 to 22 per cent tin alloy without increasing the tin contents of the slag beyond a reasonable maximum, that is to say, above $11\frac{1}{4}$ to $11\frac{1}{2}$ per cent.

The efficiency of the smelting process is determined by the following factors:

1. The percentage of tin in the rich slag and in the lead material contained in the charges.

2. The percentage of tin in the poor slag and in the lead alloy produced.

3. The form in which the various fluxes are added, that is to say in the case of iron, whether this is added as iron scrap, iron ore, cinder, scales, calcined ferruginous material, etc., while lime may be added in form of oyster shells, limestone, calcareous residues, etc.

4. The kind of lead material added, chiefly whether this consists of more or less oxidized ashes containing larger or smaller quantities of metallic lead, and the form in which the tin contents are present in this material.

5. The amount and kind of coke added.

6. The speed of operation, as influenced by the metal contents of the charge, the charging efficiency, the kind of coke used, amount and pressure of blast, draught conditions, and the degree of coarseness of the components of the charge.

7. Efficiency of smelting operations as influenced by the skill and diligence of the workmen.

8. Freedom of the metallic alloys produced from impurities such as antimony, arsenic, etc.

9. Amount and composition of the matte and speise produced.

10. The construction of the blast furnace, especially the height and diameter of the furnace.

11. Amount and quality of flue dust, and absolute loss of tin by volatilization.

While in a number of smelters the tin slags are smelted down with plain lead ashes, the all-around efficiency of the process is often improved by using lead ashes containing from 3 to 10 per cent tin, or type ashes and other material containing besides a certain amount of tin considerable quantities of antimony.

The lead-tin ashes used for this purpose are usually obtained from the last period of the lead refining process and may contain up to 10 per cent tin, but their application should only be limited to tin slags comparatively poor in tin, that is to say, such containing up to 5 per cent of tin, since with higher tin concentrations, resulting in a product of above 20 to 25 per cent tin, the poor slags obtained are too rich in tin to be discarded, requiring another smelting treatment.

The use of type ashes and similar antimonial material possesses the additional advantage of giving cleaner slags, the products obtained forming a very good base material for the production of the better grades of type metals and similarly composed alloys.

Where suitable ashes containing tin are not available, lead ashes may be smelted with tin slags for the production of a poor tin alloy holding from 3 to 5 per cent tin, which is then softened in such a way as to obtain tin ashes comparatively rich in tin. In refining lead containing appreciable percentages of tin it is comparatively easy by regulating the rate of oxidation to produce tin ashes or dross holding from 8 to 30 per cent tin. For instance, if the metallic bath is subjected to the action of an air blast, the tin ashes rarely carry more than 10 or 12 per cent tin, while if operating without blast and generally retarding the rate of oxidation, tin contents of more than 30 per cent are easily obtainable.

If lead ores are being used for this purpose, the material should be in as oxidized a condition as possible, and sulphide ores must therefore be roasted, particularly since the presence of sulphur in this process, which is often added in the form of pyrites or matte to carry down reduced iron, tends to increase the loss of tin by volatilization. For the same reason any matte used in the charge should also be added in a calcined condition. Instead of sulphides, arsenides in form of very arsenical speises or similar material should be used to take care of the metallic iron.

However, since of these two addition agents, arsenic compounds are rather more difficultly treated than sulphur compounds, many

smelters prefer to add sulphurizing agents instead of arsenides. The reason for this behavior of arsenic additions to tin blast furnace charges is the following:

If considerable amounts of speise are present in the charge, these may cause the formation of serious obstructions, a difficulty due to the fact that all the arsenic iron compounds, from Fe_2As up to Fe_4As , are exceedingly viscous and, consequently, very easily chilled. The only comparatively easily fusible iron-arsenic compound is Fe_5As . Thus, obstructions caused by chilled speise may be due to lack of iron, although an excess of iron in the speise above the proportion fixed by the formula Fe_5As will have the same effect on the fusibility of the speise produced. Since it is often quite difficult in case of trouble to quickly determine which one of the two constituents of the speise is present in excess, and since it is rather dangerous to try this out by reducing or increasing the quantity of either one of the elements, many smelters refuse to use arsenides for this purpose, in spite of the fact that the loss of tin by volatilization is slightly higher as a rule if sulphurizing agents are being used instead.

Since in smelting tin slags it is good policy in the interest of perfect reducing action to work as slowly as is compatible with satisfactory furnace efficiency, numerous smelters use a certain percentage of weak coke, such as gas coke, which tends to crumble to such an extent as to offer a certain degree of resistance to the passage of the blast air through the charge column. While fulfilling its purpose in this direction, the use of such coke material is decidedly unfavorable since, apart from containing comparatively large percentages of ashes and other harmful ingredients, the crushed coke is more or less incombustible, tending to form highly refractory coke-slag mixtures and causing the formation of serious accretions around and in front of the tuyères and within the crucible.

Much better results are obtained with charcoal which, in percentages of from 10 to 25 per cent are often added to the coke used in tin blast furnace charges. Being more friable than gas coke, charcoal serves nicely to regulate the speed of operation by adapting the percentage of charcoal added to the varying conditions of the process. The small particles of charcoal produced are easily oxidized by the blast and possess a strong reducing action on the tin and lead oxides present.

The practice of some smelters to add a certain percentage of fine coke to the charges, besides possessing the disadvantages of crushed

coke above indicated, is decidedly more objectionable in that the fine grained material tends to segregate when charged on top of the column, dropping through the coarse layers of the charge and forming comparatively heavy layers of fine coke. This is also true of the addition of fine lead or tin material which, the same as coke, is not as readily subject to blast furnace conditions as the coarse material and which, by segregating into layers, tend to clog up the furnace.

The total percentage of coke added ranges from $8\frac{1}{2}$ to 9 per cent. If charcoal is added along with the coke, the total percentage of fuel is usually increased by about $\frac{1}{2}$ per cent.

If the furnace becomes clogged with fines, the addition of larger percentages of metallic material or of more slag rich in iron will often improve conditions. The addition of fluorspar is practically useless unless the fines have become mixed with larger amounts of thick slag and speise, causing the formation of accretions along the lower parts of the furnace walls and around the tuyères. Since such accretions tend to grow at a dangerously rapid speed, it is obvious that all blast furnace operations must then be subordinated to the effort of removing them.

In accordance with their composition and their mode of formation, two principal types of tin blast furnace accretions may be distinguished, (1) those forming at the bottom of the hearth, gradually increasing in height and thickness, and developing into a steadily growing column or wall of a hard or semi-melted mixture of slag, fines, speise, metallic iron, and, eventually, tin-iron alloy, (2) those which begin to form around the tuyères, gradually closing them up entirely and which, increasing in area and thickness, continue upwards and towards the center of the furnace, decreasing the diameter of the shaft and impeding the free flow of the blast air.

The hearth accretions may be formed by excessively slow operation—insufficient pressure and volume of blast—cold working, and by the formation of iron sows or iron sow-speise mixtures. As a rule, these accretions originate in the center of the hearth, growing heavier and larger, but tending to form a bank or wall as soon as the uppermost layer of the hard deposits reaches the tuyère level, especially if the pressure of the blast is too low to carry the air currents well across the center line of the shaft.

In many instances these deposits may be removed within a comparatively short time by piercing the wall with heavy iron rods, permitting hot, fluid slag to penetrate it on all sides. The addition

of fluorspar is useful only where the accretions or deposits consist of slag or slag-fines mixtures, although better results are usually obtained in this case if a little more iron oxide is added to the charge. The arsenic contents of the charges may also be increased in order to make sure that none of the metallic iron combines with tin, forming a mixture possessing a sufficiently high melting point to cause additional trouble. If conditions are such that in spite of the presence of sufficient arsenic to form an Fe_5As compound, metallic iron continues to be formed, further addition of arsenical speise would aggravate conditions by giving rise to the formation of very viscous iron arsenic compounds richer in arsenic, and it is necessary in this case to take care of the metallic iron by adding appropriate quantities of sulphide material. This change of charge mixtures, combined with the mechanical treatment of the accretions, will remove most slag accretions, while very stubborn deposits are removed by interposing three or four straight slag charges containing maximum percentages of iron oxide and about 9 per cent of coke.

Iron sows are but difficultly removable by such and similar measures. If they become sufficiently large to interfere seriously with efficient blast furnace operation, it is best policy to empty the furnace, remove a water jacket, and to clean and repair the hearth.

The second type of blast furnace accretions originates around the tuyères. If the bright glow of the interior of the furnace is partially dimmed by a thin film of slag, the blast furnace operates satisfactorily and the tuyères should not be tampered with, except piercing the film with a steel rod once every half an hour. Indeed, this state of conditions is much more satisfactory than an unobstructed dazzling white appearance of the interior, which denotes excessively hot working and a dangerously ferruginous composition of the slag. However, this may also be due to a lack of fuel in the charges which is always indicated primarily by exceptionally hot slags evidently caused by the combustion of fine particles of metallic iron, etc., although after a short time the slag commences to show signs of chilling accompanied by rapid formation of slag accretions and general disorder.

More serious trouble is indicated by the formation of heavy layers of slag in front of the tuyère nozzles, growing in thickness and density and gradually obscuring the hot interior of the furnace from view. If repeated piercing of these accretions does not cause them

to recede, or if the holes produced by the pin close up immediately, the slag accretions have become too heavy and further use of the piercing rod would aggravate the trouble. Apart from maintaining the removed pieces of slag in a solid state, the cold blast immediately freezes fresh slag.

If only one tuyère is affected, this should be shut off from the blast by tying up the air bag; the slag accretions are then quickly melted by the heat generated by the neighboring tuyères. After the removal of the accretions, the blast must not be turned on full immediately, since heavy accretions would again be formed within a short time. It is very important, therefore, to open the air supply very little at a time, reaching the full pressure of the blast after about three to four hours.

If the disturbance in question is not limited to only one tuyère, but extends to several neighboring units, it is practically impossible, of course, to stop all of them at the same time, and the only satisfactory course to pursue in this case is to effect a radical change of charge compositions, including the following measures:

1. Exclusion of all metallic and non-metallic fines.
2. Increase of the iron oxide contents of the slag to 48–50 per cent.
3. Addition of a few shovels full of fluorspar to be deposited directly above the affected parts of the shaft.

If five or six of these charges do not produce the desired effect, three to five straight slag charges free from tin and containing about 10 per cent of coke will free the tuyères from all accretions. In contrast to lead blast furnace work, where a few heavy pieces of scrap iron are added together with the straight slag charges, this should be omitted in tin slag smelting since the high melting point of tin-iron mixtures resulting from the presence of appreciable quantities of metallic iron in the furnace would multiply the difficulties involved.

Tin blast furnaces used for this purpose may be operated with external hearth, Arentz syphon tap, or internal crucible, although in most cases internal crucible furnaces are used. In England, internal forehearth or breast pans are preferred in which slag and metal accumulate; the slag runs off by way of spout, and is collected in slag barrows and broken up when cold. From time to time the metal is run off from the breast pan into an iron pot. Speise and regulus are allowed to set in a cake on top of the metal.

Products of the Process.—The products of the tin slag smelting process are: lead-tin alloy, matte-speise, flue dust and fumes, and waste slag.

The percentage of tin in the metallic product depends upon the corresponding composition of the various materials contained in the charge and on the method of operation, and may vary from 5 to 25 per cent. Lead alloys containing less than 10 per cent tin are best subjected to a slow softening or refining process, netting refined lead and rich tin ashes running from 20 to 30 or more per cent tin. Richer lead alloys are used in the production of suitable tin-lead or tin-lead-antimony alloys, or, if contaminated with impurity, such as arsenic, copper, etc., they are subjected to a preliminary refining process—to be discussed in a separate chapter—and the pure alloy is used in the production of industrial alloys.

The matte-speise obtained in smelting tin slags with lead ashes, which always contains considerable quantities of lead and tin, is subjected to an oxidizing smelting treatment in the blast furnace. The iron is oxidized and thrown into the slag while the arsenic contents are volatilized in the metallic state or as oxide (As_2O_3). In order to prevent the contamination of the metal with some of the arsenic, sufficient metallic iron must be added to the charge, forming a small amount of thin speise comparatively poor in lead and tin.

The flue dust and fumes collected in the flue channels, if obtained in the dry state, are usually treated together with the matte-speise. If, on the other hand, the flue gases are subjected to the action of steam or water spray, the condensed fumes are obtained in form of slimes, often containing considerable amounts of chlorides. This material should be mixed with sufficient lime to neutralize and precipitate the chlorides and similar components of the slime, and the fairly dried product is briquetted and smelted with the dry flue dust and the matte-speise.

Refining of Impure Tin.—The tin produced in smelting tin residues, even if practically free from lead, is never pure, the quantity and quality of the impurities present depending upon the composition of the charge materials, as well as on the furnace conditions. The impurities usually met with in the raw tin produced from residues are: iron, copper, lead, antimony, arsenic, bismuth, and sulphur. Of these elements, iron, copper, arsenic, and sulphur are the most harmful, and the refining processes used are chiefly devised to effect the removal of these impurities, although lead and antimony, as well

as certain small percentages of tin are always scorified and removed along with those elements. It is self-evident, of course, that it is practically impossible to produce really pure tin economically and a number of so-called "refined tin" brands, especially those produced from residues, contain as high as 1 to 2 per cent impurities. A number of chemical, electrochemical, and metallurgical processes have been devised to effect purification of the blast furnace tin, but only metallurgical methods are sufficiently economical under ordinary conditions to be applicable to residue smelter conditions, unless considerable percentages of the valuable bismuth and silver are also present in the tin, when the value of the extracted metals may exceed the costs of isolation.

The metallurgical refining processes consist of repeated liquation treatments, oxidizing melting processes, and poling in melting pots, applied singly or in connection with each other. Liquation treatments alone are entirely effective where elements such as iron or copper form the chief impurities, while in presence of considerable quantities of lead and antimony (arsenic) oxidizing liquation treatments alone will give satisfactory results. Irrespective of the preliminary refining methods employed, it is always necessary to subject the tin to the poling process.

The Liquation Process of Refining.—The straight liquation process is generally carried out in small reverberatory furnaces possessing a strongly inclined long and comparatively narrow hearth. The tin ingots are placed on the highest section of the hearth, the liquated metal being collected at the other end. While the hearth of the liquation furnaces generally used for this and similar purposes is usually inclined towards the bridge, the tap hole being located at the flue end of the furnace, much better results are obtained by reversing the orders, for the following reasons:

1. Since the liquation temperature must be maintained as low and as uniform as possible, it is evident that the most favorable section of the furnace for this purpose is not that nearest to the fire-bridge, but rather the point farthest removed from it. The firing gases have to transverse the entire furnace to reach this section and are therefore much more likely to be uniform qualitatively and quantitatively without necessitating excessively sharp control of the firing.

2. It is evident that in view of the low melting point of the tin, the liquating temperatures are correspondingly low, and that, since with the common construction of liquating furnace hearths this low

temperature must be maintained at the section immediately adjoining the fire bridge, the farther end of the furnace is rarely hot enough to maintain the liquated metal in a melted condition. If, on the other hand, the liquated metal is permitted to flow towards the hottest section of the hearth, this difficulty does not exist, of course. This is particularly true if the tap is left open throughout the process, the liquated metal being permitted to leave the furnace as soon as formed. With the tap hole at the coolest point of the furnace, the metal is rarely kept sufficiently hot to pass the tap, and much work and energy is required to prevent blocking of the tap by the continually solidifying metal.

As a rule, the tap hole is kept closed throughout the liquation process, since even if it is located near the firebridge and the hearth in back of the hole is sufficiently hot, the cold air drawn through the tap hole tends to chill the thin stream of metal and to clog up the tap hole. Another serious disadvantage of the open tap hole is the fact that comparatively large amounts of solid and semi-solid foreign metals carried off by the rapidly melting tin are swept out of the furnace without being given a chance to settle out. Clogging of the tap hole can be prevented, of course, by directing a sufficiently strong flame of gas against and into the hole, but this would not prevent the mechanical impurities from being carried out of the furnace.

There is no reason, on the other hand, why these impurities could not be skimmed off in the forehearth but it is more efficient to let the liquated metal collect on the lower part of the hearth until the residues are thoroughly "dry," then to skim off the dross and pull it back over the residues. The tap hole is then pierced and the tin run into the forehearth. This method possesses the further advantage of permitting the liquated tin to be subjected to a preliminary oxidizing refining treatment. After skimming off the dross, the tin collected near the fire bridge, where it is subjected to a comparatively high heat, is puddled repeatedly and the dross formed added to the liquation residues.

After liquating the first batch of impure metal, more metal is charged on top of the residues and liquated, and the process continued until enough tin has been collected to fill the forehearth, where the metal is left to stand for a short time in order to concentrate any insoluble impurity at the surface of the bath. If lead and antimony were not contained in the raw material and the purity of

the liquated tin is high enough to be sold directly, the metal is ladled out into ingot forms, while if further refining is necessary, the metal is best left to freeze into a solid block, a large iron hook placed into the tin shortly before solidification being used to remove the block to a larger melting pot, where the metal is finish-treated by poling.

The furnace temperatures are now raised and liquation of the residues continued until a pasty and apparently non-metallic mass remains behind, which is removed and retreated with other similar material, while the impure tin liquated from the original residues is added to the next impure tin charge to be liquated.

The furnace atmosphere must be maintained pronouncedly oxidizing throughout the entire liquation process in order to assist the purification of the tin by subjecting the thin streams of liquated tin to a strong oxidizing influence.

Referring again to the question of the location of the tap hole, that is to say, to the direction of slope of the reverberatory furnace hearth, it should be mentioned in this connection, that in liquating or "drying" the residues, best results are obtained if the hearth slopes away from the fire bridge. The thin rivulets of metal emerging from the residues subjected to comparatively high temperatures always contain considerable percentages of copper and similar elements which, if the hearth slopes towards to cool end of the furnace, tend to separate out before the tin reaches the tap hole and is scraped back over the residues. It is obvious, of course, that the same argument holds good in the case of the liquation of the raw tin materials, but if the temperatures are maintained sufficiently low and uniform—an aim to be achieved in an efficient and economical manner only by removing the charge as far as possible from the fire bridge—the danger of contamination with metals or alloys of high melting points are very slight, particularly if viewed in contrast to the advantages offered by this construction of the hearth.

Further Refining by Oxidation.—If the impure tin subjected to liquation is free, or practically free, from lead and antimony, the resulting product usually is pure enough to be sold without an oxidizing refining treatment. However, in presence of these metals, alloys are being formed, the melting points of which are usually lower than that of tin.

Since certain small percentages of these elements in tin produced from residues are not objectionable as a rule, and since their removal by the oxidizing refining treatment is always accompanied by the

oxidation of corresponding quantities of tin, this process should only be applied to tin containing too large a percentage of lead and antimony to be marketable under ordinary conditions, when the excess amounts of impurities are removed by oxidation. It is impossible, of course, to economically remove all of the antimony and lead present, unless the tin contains only a few tenths of a per cent of these elements.

Where large quantities of impure tin are worked through, small reverberatory furnaces are usually employed for this purpose, while smaller amounts of liquated metal are most economically treated in connection with the liquation treatment. The liquation residues are removed and the furnace brought to dark red heat, oxidizing of the impurities being effected by frequent stirring or rabbling of the tin bath. Still better results are claimed to be obtained by using fresh wooden poles instead of rabbling tools, when the steam generated assists in the oxidizing process otherwise left to the strongly oxidizing influence of the furnace atmosphere. If the process is carried out in the liquation furnace, it is necessary to give the metal time to settle, either within the furnace or after being run into the forehearth, in order to remove any copper, iron, etc., taken up by the tin from the hearth of the liquating furnace.

Poling the Tin.—The last of the three tin refining processes which is always applied, no matter whether the oxidizing refining process is used or not, is the poling process carried out in comparatively large melting pots by means of fresh wooden poles. The melting pots used for this purpose differ from the ordinary type of melting pots used in white metal work in that their depth approximates the diameter, thus being considerably deeper than usual. The exceptional depth of these pots is necessitated by the fact that the poling treatment proper is followed by a process of settling of specifically heavier impurities, particularly the tin alloys of iron, copper and arsenic, remaining in the tin after liquation. The capacity of these tin poling pots averages 5000 to 7000 pounds.

The process is carried out as follows:

The metal bath in the pot is heated until on skimming the surface with a piece of cardboard the surface of the tin is immediately covered with a yellow to steel blue-colored skin. The metal is then poled with thin birch poles, skimming off the dross formed every 25 to 30 minutes. The time of poling depends upon the degree of purity of the metal, averaging about 4 hours with a charge of 6000 pounds.

The temperature of the metal must be maintained uniform throughout the poling process.

While on one hand, poling causes the oxidation of the bulk of the lead, antimony, bismuth, and arsenic present in the tin, it decomposes and reduces lower and higher oxides, as well as sulphides contained in the metal, permitting these elements to form alloys with the tin which, on account of their higher specific gravities, will settle down and concentrate at the bottom of the pot.

After poling, the metal is skimmed and left to cool down to just above its freezing point when, on skimming the surface with a piece of cardboard, it will retain a mirror-like appearance for some time. The tin is then left to stand quietly at this temperature for two hours, the dross formed skimmed off, and the metal ladled out carefully and without causing agitation, which would cause the lower layer of specifically heavier tin alloys to be washed back into the refined tin. An experienced man will easily get the "feel" of the difference of fluidity, which is similar to that noticed in the case of efficiently treated remelted zinc where the zinc-lead alloy collecting at the bottom of the pots represents the heavier and more viscous layer.

As soon as the ladle approaches this layer, pouring of the tin is stopped, and the tin already ladled out is marked as first refined tin. It is obvious, of course, that this tin is not perfectly pure, and if lead and antimony are present in the raw tin material, a small percentage of these elements is bound to be retained by the refined tin. This cannot be removed economically by any other metallurgical process.

The impure metal forming the lower layer of the contents of the poling pots is also ladled out and the ingots set aside until enough of this metal has been collected to make one or several charges. These are then melted down in a large pot, subjected to poling and segregation—the same as the semi-refined tin—and a further quantity of refined tin obtained, while the impure layer obtained from this remelting process is ladled out and added to a charge of raw tin material subjected to the liquating process in a reverberatory furnace.

Influence of the Impurities of Tin.—It may generally be stated that of the various impurities of tin, iron, arsenic, sulphur, antimony, bismuth, lead, and copper, none exert a noticeably favorable influence on the mechanical properties of this metal. Of the few deter-

mined attempts to ascertain the exact degrees of influence exerted by the commoner impurities, those carried out for the English Smelting Works, Capper Pass & Sons, are by far the most exhaustive and authoritative, and it will be interesting, therefore, to outline the results obtained as far as these are of interest to the metallurgist.

The following qualities of tin were subjected to the experiments:

TABLE 1

	Pb	Sb	Cu	Bi	As	S	Fe	Zn	Ag Au
1	.0025	.0031	.0004	.0004	.0000	.0002	.0016	.0000	.0000
2	.0371	.0210	.0014	.0048	.0113	.0015	.0170	.0000	.0000
3	.0380	.0400	.0120	.0030	.0500	.0000	.0020	trace	.0000
4	.0600	.0233	.0360	.0030	.0500	.0060	.0110	.0000	.0010
5	.0110		.0020	.0020	.0020	.0040	.2060	.0000	.0000
6	.0580	.0200	.0740	.1600	.0150	.0030	.0070	.0000	.0140
7	.7140	.0200	.0160	.0560	.0000	.0010	.0050	.0000	.0140
8	.1570	.0740	.2740	.3300	.1000	.0040	.0050	.0000	.0040
9	.1540	.1100	.4730	.0700	.0300	.0040	.0380	.0030	.0100

Apart from this series of original tin samples another series was prepared by adding certain amounts of impurities to the original tin sample No. 1 (Table 2).

TABLE 2

	Per Cent		Per Cent		Per Cent		Per Cent
1a	0.048 Pb	1e	0.012 Cu	1i	0.008 As	1n	0.011 Fe
1b	0.253 Pb	1f	0.050 Cu	1k	0.055 As	1o	0.058 Fe
1c	0.048 Sb	1g	0.012 Bi	1l	0.005 S	1p	0.040 Zn
1d	0.243 Sb	1h	0.056 Bi	1m	0.036 S	1q	0.240 Zn

The experiments were carried out along the following lines:

1. Influence of the various impurities on the mechanical properties of tin.
2. Influence on the melting points.
3. Influence on the specific weight.
4. Influence on the formation of dross.

The experimental results obtained are shown in Table 3.

TABLE 3.—INFLUENCE OF VARIOUS IMPURITIES ON THE PROPERTIES OF TIN.

	Hard- ness, Brinell	Contraction, Per Cent	Specific Weight	Dross, Per Cent		Hard- ness, Brinell	Contraction, Per Cent	Specific Weight	Dross, Per Cent
1	5.4	100	7.286	1.7	1n	5.4	100		1.5
1a	4.5	100		1.8	1o	5.7	100	7.297	2.6
1b	6.7	95	7.298	1.8	1p	5.8	100		2.0
1c	5.3	100		1.6	1q	11.8	74	7.286	3.6
1d	5.8	100	7.290	2.3	2	8.8	96	7.297	2.7
1e	4.4	100		...	3	9.6	94	7.297	2.2
1f	5.3	98	7.288	...	4	8.1	94	7.298	1.9
1g	5.9	100		1.5	5	5.5	100	7.295	2.9
1h	4.6	100	7.283	2.2	6	9.9	90	7.291	2.5
1i	7.8	100		2.0	7	9.6	54	7.321	1.7
1k	8.7	96	7.281	1.9	8	12.8	77	7.308	2.4
1l	5.4	100		1.5	9	17.0	69	7.302	2.6
1m	6.0	100	7.286	2.3					

1. The results obtained show that, while in general the hardness of tin is increased by traces of impurities, small percentages of lead and copper exert a noticeable softening influence, although larger quantities of these impurities cause a corresponding increase of hardness. Of particularly hardening influence are arsenic and zinc. The high hardness figures of samples 2, 3, and 4 are caused by the higher percentages of arsenic, those of sample 6 by the relatively higher amounts of impurities generally.

2. Most of the impurities of tin, excepting antimony and sulphur, tend to lower the melting point of tin. This fact goes to show that the presence of impurities in tin is indicated by lower as well as higher melting points. Pure tin melts at 232° C. sharp, while in presence of impurities, the sharpness of the melting point is more or less diminished, fluctuating within several degrees of the melting point of pure tin. The melting points of the comparatively pure samples 1, 2, 3, 4, 5, and 6 range within 0.3° C., while the more common qualities 7, 8, and 9 melt at somewhat lower temperatures. The lowest melting point is exhibited by sample 2, which melts 3° C. below the melting point of sample 1, the purest tin of the series.

The specific weights of tin also are influenced both ways, depend-

ing on the nature and the quantity of impurities present. Lead, antimony, copper, and iron increase the specific weight of tin, which is lowered by traces of bismuth and arsenic, while traces of sulphur and zinc do not influence the specific weight in either direction. These results show that the specific weight of a given brand of tin does not indicate its purity, as is often believed to be the case.

One of the most important items covered by this series of experiments is the amount of drossing induced by the various impurities contained in pure and impure brands of tin. Wherever tin is being melted, a certain amount of dross is bound to be produced, especially where the melting appliances used are inefficiently constructed or operated. Since most of the impurities present in commercially pure tin are more easily oxidized than the tin itself, the drosses are always considerably stronger contaminated than the metallic tin, thus effecting a corresponding reduction of value without, on the other hand, increasing the market value of the tin.

Table 3 shows that even the purest quality of tin forms dross on melting, while some metallic impurities, such as zinc, are particularly active in increasing the amount of dross formed. Iron also tends to produce larger quantities of dross.

Lead both in small or large quantities does not influence the formation of dross or the amount of dross formed. Small amounts of antimony and bismuth do not produce any effect, while larger percentages of these elements tend strongly to increase the amount of dross formed.

CHAPTER II

THE WHITE METAL ALLOYS

White metal alloys, generally termed white metals, whether composed of only one or of any number of white metals mixed, or alloyed with each other, are commonly understood to consist chiefly of the binary or ternary alloys of tin, lead and antimony, containing a number of other metals such as copper, zinc, bismuth, arsenic, etc., added to improve or modify the property of the alloys to better suit the various purposes in question.

The most important groups of this type of alloys are the white bearing metals, solders, type metals, fuse metals, accumulator alloys, bullet metals, special alloys for the chemical industry, and the various soft and hard alloys used for the production of castings.

Because of the extraordinary importance of these alloys in practically all branches of industry, the subject of white metals constitutes a most important section of the alloy producing industries, and since the suitability of these alloys for their various purposes is to a large extent governed by correct composition, absence of impurities, and a number of other metallurgical factors, the discussion of the production and treatment of the white metal alloys should be preceded by a study of the mechanical and physical principles determining the suitability of these alloys for their respective purposes.

WHITE BEARING METALS

Since in perfectly lubricated and adjusted bearings, shaft and bearing are always separated by a thin film of oil, so that friction is merely limited to that set up between a solid and a liquid, the nature of the bearing metal employed is of little or no consequence as long as this is able to bear the general mechanical strain imposed by the weight of the shaft and the vibratory shocks of the system. However, perfectly ideal conditions are not attainable in actual practice, and it is necessary, therefore, to provide a bearing metal hard

and strong enough to withstand the considerable mechanical strains, to be sufficiently plastic to adjust its shape to incorrect adjustment, and highly susceptible to polishing so as to offer a minimum of friction. It is also necessary that these properties are maintained at the elevated temperatures of bearings under actual service conditions. These requirements are best defined by the five essential characteristics of bearing metals stated by Dr. Dudley.¹

1. The metal must have the strength necessary to sustain the loads ordinarily imposed on it.

2. The metal must not heat rapidly.

3. It must work well in the foundry.

4. The coefficient of friction must be small.

5. The period of wear must be long in comparison with the amount of material actually worn off the surface.

Considering the results of numerous investigations of the constitution and the properties of bearing metals by authorities such as Charpy, Clamer, Heyn and Bauer, and Behrens and Bauke, the following deductions are in order:

In the first place, the white bearing metals must be sufficiently soft to adapt themselves to the shape and the movement of the rotating shaft, and to take up and distribute the pressure uniformly. For this reason, these alloys must be rich in tin or lead, and correspondingly poor in antimony and copper, depending on conditions.

Good bearing metals must also be sufficiently hard in order to attain a favorable coefficient of friction and a high degree of resistance, as well as to stand up under the load of the shaft, a requirement which, in the case of the white bearing metals, accounts for the greater suitability of alloys rich in tin, since these are considerably harder than lead-base bearing metals. In view of the unavoidable impact strains suffered by bearings, this hardness must not be accompanied by too high a degree of brittleness, that is to say, the bearing metal must be sufficiently tenacious to withstand the pressure and the shocks involved. The higher the tin contents of white bearing metals, and the lower the percentage of antimony contained above a certain minimum content, the more tenacious the alloys.

The heat conductivity of bearing metals must be high, without, however, endangering the bushings. The higher the specific heat and the lower the atomic weight of these alloys, the cooler the bearings.

¹ Journal of the Franklin Institute, Feb., 1892.

It is obvious that since properties such as hardness, softness, plasticity, toughness, etc., cannot be united within one metal or any one homogeneous alloy, forming solid solutions, heterogeneous alloys consisting of a soft matrix with hard crystals embedded in it, or a hard metal interspersed with veins of a softer constituent represent ideal bearing metals. The load is then carried by the hard grains possessing a low coefficient of friction, and which are not easily cut, while the plastic matrix permits the bearing to adjust itself closely around the shaft, or even to readjust itself to changing points of pressure, thus avoiding excessive local pressures, which are the main cause of practically all failures of bearings. Another advantage of mottled bearing surfaces, in which the harder constituents stand out in slight relief, is that the large number of canals and pools thus formed serve to retain the oil film and to promote the spreading of the lubricant over the surface.

These chief properties of bearing metals are not reserved to white metal alloys alone, of course, and the following groups of alloys have found practical application for this purpose:

1. Tin-base bearing metals, consisting essentially of tin, and containing various percentages of antimony and copper, in which hard particles of SbSn and SbCu_2 are embedded in the tin-rich eutectic.

2. Lead-base bearing metals, containing, besides lead, smaller quantities of tin and antimony. The hard compound SbSn is embedded in the softer matrix.

3. Copper-tin (zinc) alloys, used for high pressures and strong impacts, especially at elevated temperatures, in which the hard compound SnCu_3 is embedded in a softer solid solution of copper and tin. If phosphorus is also present in the alloy, a hard compound PCu_3 is formed.

4. Copper-Tin alloys, containing appreciable percentages of lead, which confers a high degree of plasticity to the hard alloys.

5. Tin-Antimony-Zinc alloys, used where cheapness is an important requirement.

6. Other special alloys, particularly self-lubricating alloys.

Tin-Base Bearing Metals.—Compared with the other white bearing metal compositions, tin-base alloys possess the following chief advantages:

While soft enough to adapt themselves to the rotating shaft, and sufficiently hard to be durable and to possess a comparatively low

coefficient of friction, the matrix of tin-base alloys is much tougher than that of bearing metals rich in lead, rendering them more resistant against shocks and vibrations.

They do not tend to stick to the shafts, as is the case with lower grade bearing metals, and for high speeds of revolution, as, for instance, in turbines, as well as for heavy loads, bearing metal alloys containing from 75 to 85 per cent of tin are required.

Tin-base alloys give cooler bearings, and since high speed bearings and those subjected to greater pressures, heat more, the percentage of tin contained should be correspondingly high.

They are considerably less viscous than the lead-base alloys, their tendency towards the formation of blow holes being correspondingly smaller.

They are more fluid and are thus able to cover a large area in a thin layer. Table 4 gives the composition of most of the important tin-base bearing metals used for the various purposes in this and other countries.

Considering the variety of application and their suitability under practically all conditions, tin-base bearing metals doubtlessly constitute the most important group of bearing metals.

Theoretically, the chief requirements of a bearing metal, that is, the presence of hard compounds embedded in a soft matrix, could be met by plain tin-antimony alloys, containing from 8 to 10 per cent antimony. However, the hard compound existing in these alloys, the cuboids of the tin-antimony compound, SbSn , which begin to solidify at above 530° Fahr., will float, thus producing an alloy, which is too hard and brittle at the top, and too soft at the bottom. The proper proportion of hard compounds to soft and ductile matrix would not in this case be in evidence at the surface of the bearing, where it is required in the first place.

On cooling a fused tin-antimony alloy, containing sufficient percentages of copper, dendritic crystals holding from 30 to 40 per cent copper are first crystallized out, which, according to Heyn and Bauer,¹ may be regarded as representing mixed crystals of copper and tin. In relatively thin layers of metal such as are represented by the bearing metal shell, these separated crystals form a lattice system throughout the whole of the mass of metal, thus preventing the segregation of the antimony cuboids. After the separation of the copper-base alloy crystals, "antimony cubes" commence to appear. They

¹ Heyn and Bauer, *Mitteilungen a.d. Materialpruefungsamt*, 1911, p. 29.

TABLE 4.—TIN-BASE BEARING METALS

Purpose (Name)	Per Cent Sn	Per Cent Sb	Per Cent Cu	Per Cent Pb	Per Cent
Thurston's B.M.....	70.7	19.5	9.8		
French Ry.....	71.0	24.0	5.0		
Ludenscheidt (Germ.).....	71.8	24.3	3.85		
Prussian Ry.....	72.0	26.0	2.0		
British Ry. (Medium).....	72.0	26.0	2.0		
Natke's, Heavy Axles.....	72.7	18.2	9.1		
Heavy Ry. Axles.....	72.8	18.0	9.2		
Prussian Ry.....	73.0	18.0	9.0		
French Western Ry.....	73.0	12.0	8.0	7.0	
Husman's.....	73.9	11.3	4.3	10.0	0.4 Zn
Prussian Ry.....	74.0	15.0	11.0		0.18 Zn
German (Light Loads).....	76.0	17.0	7.0		
Richard's.....	76.0	12.7	8.5	2.8	
English Ry.....	76.7	18.5	5.8		
	77.5	11.2	10.0	0.75	
Crank-shafts.....	78.0	10.0	12.0		
Swiss Ry.....	80.0	10.0	10.0		
Portuguese Ry.....	80.0	12.0		8.0	
German (Light Loads).....	80.0	12.0	8.0		
Danish Ry.....	80.0	11.0	9.0		
Navy Bearing Metal (Hard).....	80.0	15.0	5.0		
French Colonial Ry.....	80.0	13.0	7.0		
German Standard.....	80.0	12.0	6.0	2.0	
German Standard.....	80.0	10.0	10.0		
Chilean Ry.....	80.0	10.0	10.0		
	80.9	10.7	4.2	3.3	
General Bearing Metal.....	81.0		5.0	14.0	
Piston.....	81.0	12.5	6.5		
General Bearing.....	81.0	14.0	5.0		
Bolley's B.M.....	81.3	12.5	6.2		
Dutch Ry.....	81.5	8.8	9.6	Trace	
Valve Rods, Etc.....	82.0	10.0	8.0		
Western Austrian Ry.....	82.0	12.0	6.0		
French Ry.....	82.0	12.0	6.0		
Electr. Ry. Motors.....	82.0	14.0	4.0		
German (Light Loads).....	82.0	11.0	7.0		
Dutch Rys.....	82.0	9.0	9.0		
Richards Plastic Babbitt.....	82.43	9.47	8.1		
Berlin Ry.....	83.0	11.0	6.0		
Admiralty Special.....	83.0	9.0	8.0		
German Ry.....	83.0	11.0	6.0		
French Northern Ry.....	83.0	10.5	6.5		
Distributing Slide Valves.....	83.2	11.2	5.6		
Portuguese Ry.....	83.3	11.1	5.6		
	83.3	11.0	3.9	0.9	
French Eastern Ry.....	83.3	11.11	5.55		
French Car Bearings.....	83.3	11.1	5.5		
Gemma's, Axles.....	83.3	11.11	5.55		
Hard Babbitt.....	83.3	8.3	8.4		
Prussian State Ry.....	83.4	11.0	5.6		
Calumet & Hecla A.C.1.....	83.5	11.0	5.5		

TABLE 4—Continued

Purpose (Name)	Per Cent Sn	Per Cent Sb	Per Cent Cu	Per Cent Pb	Per Cent
Motor Bronze B.M.....	84.0	7.5	7.5		1.0 Bi
Babbitt Metal.....	84.0	9.0	7.0		
Gemma B.M. (Heavy Loads).....	84.0	7.7	2.7 ⇐	5.6	
North German Lloyd.....	84.47	0.94	4.82	8.94	1.15 Zn
English Admiralty, Plastic.....	85.0	10.0	5.0		
German Admiralty.....	85.0	7.5	7.5		
Motor Metal.....	85.0	8.25	8.25		
Jacobi Metal.....	85.0	10.0	5.0		
Kamarsch's B.M.....	85.0	5.0	3.6	 {	1.6 Bi
Original Babbitt.....	85.0	12.0	3.0		1.4 Zn
Street Car Motors.....	85.0	10.0	5.0		
Spanish Ry.....	86.0	9.0	3.25		1.75 Zn
S.A.E. Nr. 11.....	86-89	6-7.5	5-6.5	2.35	
Original Babbitt.....	86.0	9.0	5.0		
	86.3	10.3	3.2		
Russian Ry.....	86.3	6.95	2.82	3.66	0.82 Fe
German Ry. (Heavy Loads).....	86.81	7.62	5.57		
For Heavy Loads, Hiorns.....	87.0	7.0	6.0		
American Automobile.....	87.0	7.0	6.0		
	87.3	7.5	4.6	0.62	
Karmarsch's S.B.M.....	87.5		12.5	1.2	
Custan's B.M.....	87.5	1.0	11.5		
Original Babbitt.....	88.8	7.5	3.5		
Karmarsch's B.M.....	88.8	7.4	3.7		
U. S. Govmt. Friction.....	88.8	7.5	3.7		
Original Babbitt.....	88.9	7.4	3.7		
American Automobile.....	88.9	7.4	3.7		
Genuine Babbitt.....	89.0	7.5	3.5		
Navy Bearing Metal.....	89.0	7.3	3.7		
Original Babbitt.....	89.0	9.0	2.0		
American Automobile.....	89.0	7.0	4.0		
Genuine Babbitt for Heavy Service.....	89.0	8.0	3.0		
American Automobile.....	89.3	8.9	1.8		
English Marine B.....	89.71	Trace	4.22	5.65	0.42 Zn
	89.9	4.3	4.2	1.3	
Heavy work, Hiorns.....	90.0	8.0	2.0		
Fahrig's B.M.....	90.0		10.0		
Russian Ry. (Cars).....	90.0	8.0	2.0		
S.A.E. Nr. 10.....	90-92	4-5	4-5	2.35	
Russian Ry.....	90.0	8.0	2.0		
Prussian Ry.....	90.0	6.0	4.0		
Austrian Ry.....	90.0	7.0	3.0		
Bavarian Ry.....	90.0	8.0	2.0		
Navy Bearing.....	91.0	4.5	4.5		
Prussian Ry.....	91.0	6.0	3.0		
International Aircrafts.....					
Standard Board.....	91.0	4.5	4.5		
Oriental Ry.....	91.7	6.0	3.3		
Zeppelins.....	92.4		3.9	3.7	
Dudley's Antifriction.....	98.13		1.6	0.25	

are essentially mixed crystals composed of approximately equal parts of tin and antimony, but will also take up considerable percentages of copper, varying from 5 to 6 per cent. By separating pure cuboid crystals from a solidifying bearing metal alloy rich in copper, Heyn and Bauer were able to determine the following composition:

50.4% Antimony,
43.5% Tin,
5.3% Copper.

Since typical tin-base bearing metals are mechanically weak, they must be cast in shells of stronger metals such as iron, while for very small bearings comparatively heavy white metal bearings are used without shells.

The superior bearing properties of tin-base alloys, that is, (1) a higher degree of both hardness and toughness, improving the wearing qualities, (2) retention of superior qualities at elevated temperatures, (3) cooler operation, (4) freedom from stickiness, (5) lower viscosity and greater fluidity than lead-base alloy, are more or less influenced by a number of impurities, although the general opinions held concerning one or the other foreign element present in tin-base bearing alloys are gradually being disproved by modern research and experience. Of the numerous impurities or foreign ingredients—intentional or unintentional—lead, iron, nickel, and zinc are the most important.

Lead is present in practically all tin-base bearing metals, small quantities of this element increasing the elongation of the alloys and their resistance against rapid fluctuations of load. In America, lead to the amount of not more than 0.35 per cent is permitted as a general rule, while occasionally, percentages of up to 0.75 per cent are tolerated. Alloys containing more than 1 per cent lead are generally considered useless for high grade work, the chief reasons believed to be responsible for this attitude being the lowered resistance of the bearings against the corrosive influence of lubricants containing an excessive amount of alkalis, the decreased ductility and tenacity of the alloys, and the rapidly increasing tendency to develop cracks at relatively moderate loads. This does not apply to the innumerable babbitt metals, of course, which contain from 4 to 8 or even more per cent lead, but it appears that the maximum of 0.50 to 1.00 per cent lead set for the high grade tin-base bearing metals referred to here is rather low. Comprehensive experiments and careful observation of practical results obtained with such alloys

containing from 0.60 to 1.5 per cent lead have shown, that if these mixtures are melted and poured correctly very satisfactory results may be obtained even under the most trying operating conditions.

A very interesting series of experiments were carried out by English authorities with nine tin-base alloys containing varying percentages of lead, and poured at different temperatures, to test their suitability for automobile motors.¹ Table 5 gives the composition of the alloys, the pouring and annealing temperatures applied, and the Brinell hardnesses determined.

TABLE 5.—PROPERTIES OF SOME TIN-BASE BEARING METALS.

Number of Alloy	Per Cent Sn	Per Cent Sb	Per Cent Cu	Per Cent Pb	Per Cent Ni	Pouring Temperature, Degrees C.	Annealing Temperature, Degrees C.	Hardness Brinell
1	90.8	4.1	3.8	1.02		370	150	26
2	83.3	11.0	3.9	0.92		350	150	28
3	80.9	10.7	4.2	3.3		350	150	31
4	89.9	4.3	4.2	1.3		370	150	30
5	86.3	10.3	3.2	0.0		400	150	30
6	60.2	12.0	6.3	19.9		400	150	34
7	90.8	4.3	3.9	Tr.	0.53	350	150	20
8	87.3	7.5	4.6	0.62		400	150	33
9	77.5	11.2	10.0	0.75		400	150	31

The values for the coefficients of friction fluctuated between 0.002 and 0.006, depending on the composition of the metal and the pouring temperatures observed.

The tests were maintained for very long periods and under widely differing loads, and the following results were obtained:

Alloy No. 1, containing 1.02 per cent lead, proved to be the most suitable, standing up under extraordinarily high loads without cracking or suffering excessive deformation, the coefficient of friction remaining very low throughout. Alloy No. 8 proved to be second best, standing up very well under ordinary loads, and running hot for about 1 hour before melting. Next in order was alloy No. 9, the suitability of which under the testing conditions applied proved to

¹ Metal Industry, London, Vol. 23, pp. 148 and 170.

be much less satisfactory. Alloy No. 4 did not stand up well under higher loads, running after 75 minutes, but showing a particularly low coefficient of friction. The alloys No. 3, 5, 2, 6, and 7 exhibited too high a coefficient of friction to be useful for the exacting work in question, running out after as short a testing period as 40 to 45 minutes.

Tin-base bearing alloys containing from 4 to 30 per cent lead are being used for practically every purpose, including maximum loads (locomotives) and very high speeds (turbines). An alloy composed of

80% Sn, 11% Sb, 3% Cu, 6% Pb

is very useful for Diesel engines, turbines, rolling mills, and locomotives. Another, cheaper alloy containing

60% Sn, 10% Sb, 1.5% Cu, 28.5% Pb

may be used for internal combustion engines of all types, steam engines, dynamos, locomotives, etc.

The influence of *Nickel* on tin-base bearing metals appears still to be a subject of profound controversy. According to Munday and Bissett,¹ it seems that the original idea of adding nickel to these alloys was not a strictly metallurgical one, designed to improve the bearing qualities of the alloys, but to serve as means of identification of a certain manufacturer's product after the bearing had been cast and taken into service, whether with success or otherwise. This practice was then adopted by other manufacturers, and since very satisfactory alloys were also given small percentages of nickel, one or the other outstanding virtue of such alloys became gradually to be attributed to the nickel contents. The general opinion concerning small percentages of nickel, not exceeding 0.5 per cent, is that while improving elongation and eliminating the tendency towards cracking, this element does not interfere with the good wearing qualities of the alloys. The outstanding disadvantage is said to be the decrease of Brinell hardness, or, in other words, the decreasing resistance against deformation of the bearing under heavy loads. It is interesting, indeed, to find, that the experiments of Munday and Bissett, carried out with an alloy composed of 93 per cent tin, 3.5 per cent antimony, and 3.5 per cent copper proves that the addition of nickel to alloys of this character does not yield substantial advantages, and that some valuable properties are diminished. Table 6 gives some

¹ Brass World, 1924, p. 15.

of the mechanical values obtained with this tin-base alloy containing 0.1, 0.2, 0.3, 0.4, 0.5, and 1.0 per cent nickel.

TABLE 6.—PROPERTIES OF TIN-BASE BEARING METALS CONTAINING NICKEL.

Per Cent Ni	Tensile Strength, tons per Square Inch	Elongation (2 In.) Per Cent	Hardness, Brinell No.	Yield Point, 0.001 In.	Final Length, fr. 0.5 In.
0.0	5.12	11.6	24.9	3.569	
0.1	4.6	18.0	19.3	2.85	0.235
0.2	4.6	12.2	21.5	2.85	0.223
0.3	4.4	6.1	22.3	2.57	0.25
0.4	4.6	11.0	21.5	3.0	0.218
0.5	3.6	5.7	21.5	3.07	0.242
1.0	4.1	15.4	20.1	2.57	0.242
Also 4.0 per cent copper.					

In all tests the nickel was made to replace the tin, the copper contents remaining constant. The nickel was introduced in the form of cupro-nickel, containing 20 per cent nickel. The tensile and other test pieces were poured at 480° Fahr. (350° C.) and cast into iron molds heated uniformly to 212° Fahr. (100° C.). The Brinell test was with a 500 kg. load, 10 mm. ball. The compression tests were made with test pieces 0.5 in. high and 0.564 in. in diameter.

Actual running tests made with these alloys proved to be fairly satisfactory. The loss of hardness due to rise of temperatures is practically uniform with all percentages of nickel, amounting to 0.7 points (Brinell Numbers) at 105° Fahr., 1.2 to 1.3 points at 150° Fahr., and 1.9 to 2.1 points at 230° Fahr.

The conclusions drawn from the results of these tests are that the presence of small quantities of nickel in tin-base bearing alloys appears to have the effect of combining with, or dissolving in, the copper present, and that the copper-tin compound is suppressed. The alloy therefore loses that valuable property of resistance to crushing which it appears to owe to the interlocking of the copper-tin compound in its dendritic form, and the hardening effect, if any, of the nickel does not compensate for the loss of this form of structure.

Bismuth in traces is sometimes added as flux and does not influence the pouring and bearing qualities in any way. Larger quanti-

ties are occasionally added to tin-base bearing metals used for high speed operation, as, for instance, in motors, dynamos, etc. Table 7 gives a few alloys containing bismuth as a potential constituent.

TABLE 7.—TIN-BASE BEARING METALS CONTAINING BISMUTH.

Purposes (Names)	Per Cent Sn	Per Cent Sb	Per Cent Cu	Per Cent Bi	Per Cent Zn
For Dynamos.....	88.0	8.0	3.5	0.5	
Kamarsch's B.M.....	85.0	5.0	3.6	1.6	1.4
Motor Bronze.....	84.0	7.5	7.5	1.0	

It appears that the addition of small percentages of bismuth tends to increase the hardness of the alloy without causing a corresponding increase of the brittleness.

Iron in any amount increases both hardness and brittleness and must therefore be considered an absolutely undesirable constituent.

Zinc, while generally considered an undesirable constituent of tin-base bearing metals, is used by a number of Continental Railroads and Shipping Companies as a component of tin-base bearing alloy for heavy loads. (See Table 4.) It is well known that under ordinary conditions, zinc increases the hardness as well as the brittleness of the bearing metals, but there can be no doubt that with proper methods of casting and treating, the brittleness of the alloys is not affected while the increase of hardness induced remains unimpaired.

Influence of Casting Temperatures on the Bearing Properties.— Apart from the composition of bearing metals and the manner of lubrication, the following factors are of pronounced influence on the bearing qualities of these alloys:

1. Length of melting period,
2. Maximum temperature reached during melting of the alloy,
3. Casting temperature of bearing metals,
4. Temperature of the molds,
5. Rate of cooling.

The influence of the length of the melting period on the quality of bearing alloys is obviously due to the increasing rate of oxidation, especially if the melting temperature, or rather the maximum tem-

perature reached during melting, exceeds the critical temperature; while varying with the composition of the alloys, this may be assumed to range about 125° Fahr. (50° C.) above the freezing temperature.

The casting temperature of the metal and the molds determine the rate of cooling, which, in turn, determines the formation of the structure, that is to say, the size of the hard compounds and their relation to the matrix and the mechanical stresses. The lower the rate of cooling the larger the hard tin-copper and tin-antimony crystals, and since at an equal proportion by weight of the hard compounds the larger crystals possess a relatively much smaller surface, the bearing strength of the total of these crystals is correspondingly smaller than that exhibited by an equivalent amount—by weight—of smaller crystals. The casting temperature of the bearing metal must therefore be high enough to completely fill the mold or the bearing with perfectly fluid metal, but not so high as to cause excessive oxidation—insignificant though it may appear to the naked eye—and to heat up the mold to a temperature which would prevent sufficiently rapid cooling of the bearing metal.

Too rapid cooling of the bearing metal, on the other hand, prevents sufficiently perfect separation of the hard particles from the matrix.

The temperature of the mold is of some importance in that, while preheating is required in order to cause the shell to contract with the white metal, giving it a better adhesion, this preheating temperature must not exceed the maximum degree required, so as not to interfere with sufficiently rapid cooling of the bearing.

Apart from the direct influence of the rate of cooling on the size of the hard particles, its effect on the mechanical properties of the softer matrix also are of importance. The experimental work carried out by Behrens and Bauke¹ have shown that the hardness of the matrix of bearing metal alloys varies with the rate of cooling. In rapidly cooled alloys the hard constituents do not get time to separate out as completely as at lower rates of cooling, so that the matrix solidifies with a greater percentage of copper and antimony. While in rapidly cooled alloys the hardness may reach 2, that of tin being 1.7, it may be as low as 1.6 in slowly cooled material.

Experiments, reported by R. T. Rolfe,² carried out with Admiralty

¹ Baumaterialienkunde, 1899.

² Rolfe, "Babbitt Metal, Its Origin and History" (The H. J. Humphries & Cooper Smelt. Corp.).

alloy, containing 85 per cent tin, 6.5 per cent copper and 8.5 per cent antimony, and cast at various temperatures into molds preheated to different degrees of heat, yielded the results given in Table 8.

TABLE 8

Casting Temperature, Degrees C.	Brinell Hardness at a Mold Temperature of			
	15° C.	100° C.	200° C.	300° C.
300	32.8	31.2	28.4	29.8
365	25.4	26.5	29.8	28.4
425		35.3	32.8	31.2
495		34.4	31.2	29.8

Lead-base Bearing Alloys.—In contrast to the commonly accepted view of engineers, lead-base bearing metals, if properly compounded, have been found to possess practically all of the properties of tin-base bearing metals, especially where resistance against heavy loads and increased temperatures form chief requirements. Alloyed with special elements such as bismuth, these alloys are also being used successfully for high speed bearings. Lead-base bearing metal alloys are being used extensively on Continental Railroads, for all kinds of machinery, on automobiles, etc. In their relation to pressure and speed, good lead-base alloys may be said to represent very useful bearing metals for heavy pressure and medium speed, or for medium pressure and high speed. Alloys of this type should contain from 30 to 40 per cent tin, while cheaper alloys containing from 15 to 25 per cent tin render satisfactory service under medium pressures at medium speed, or under light pressures at high speed. Wherever the bearings have to stand up under heavy loads and high speeds, lead-base alloys should not be used.

It is a peculiar fact, which has given rise to many serious misunderstandings concerning the value of lead-base alloys as compared to bearing metals rich in tin, that while frequently the alloys of this group give results equal, if not superior, to tin-base alloys, other mixtures of exactly the same composition may prove to be entirely useless for much less exacting services. This phenomenon is exclusively due to the far greater susceptibility of lead-base alloys to the

influence of pouring temperatures, the range of temperature necessary to yield best results being comparatively small.

The superiority of tin-base alloys over lead-base bearing metals for a number of purposes is based on the following differences of properties:

1. Tin-base alloys are considerably harder without being correspondingly brittle and possess a much higher compressive strength.

2. Their wearing qualities are superior, while due to the lower melting point of the hard particles of lead-base alloys, tin-base metals stand up much better under severe bearing pressures at elevated temperatures.

Other points of superiority of tin-base alloys have been enumerated on page 47.

Constitution of Lead-base Bearing Metals.—The constitution of the lead-antimony-tin alloys has been studied by Campbell,¹ Loebe² and Heyn and Bauer.³ The ternary diagram of this group of alloys in combination with the corresponding binary diagrams of the three components is shown in Figure 16.

It will be found that while the tin-base alloys range about point VI (Figure 16), the lead-base alloys are concentrated near point VIII, representing one of the eutectics of the ternary lead-tin-antimony alloys. A study of the diagram yields all the necessary information concerning the melting and freezing points of the ternary alloys, together with the various forms of crystallization. Thus, all the compositions lying within the field I-II-VIII commence to melt at the temperatures indicated in the diagram, the first components crystallizing out being antimony crystals containing tin in solid solution. When on further cooling a temperature of 247° C.—point VIII—is reached the melt solidifies, forming the eutectic $\text{Pb} + \text{Sb}$. In the case of alloys belonging to the group of compositions covered by the field I-VII-VII antimony crystals, holding tin in solid solution are also separated out first until line VII-VIII is reached when the hard compound SbSn begins to be formed. Cooling proceeds along the line VII-VIII until at 247° C.—point VIII—the eutectic $\text{Pb} + \text{SbSn}$ solidifies.

The field VII-VIII-IX includes the composition of numerous bearing metals containing from 20 to 60 per cent tin, from 5 to 20 per

¹ School of Mines Quarterly, 1911, p. 244.

² Metallurgie, 1911, p. 7.

³ Untersuchungen über Lagermetalle, 1914, p. 21.

cent antimony, and from 75 to 3 per cent lead. On cooling down a fused alloy belonging to this group, the white cuboids SbSn crystallize out first until the line VIII-IX is reached, when the eutectic $\text{SbSn} + \text{Pb}$ commences to solidify. On reaching point IX, a second eutectic, $\text{Pb} + \text{Sn}$, solidifies.

Many of the alloys forming the tin-base bearing metals may be found in field VII-IX-VI. The cuboids SbSn are first separated. On reaching the line IX-VI, tin-mixed crystals, containing not more than 10 per cent antimony in solid solution, begin to separate out from the melt, while the eutectic, $\text{Pb} + \text{Sn}$, solidifies on line IX-IV.

All the alloys covered by the neighboring fields VII-VIII-IX and VII-IX-V tend strongly to segregation, the SbSn cuboids separated out first, rising to the surface of the bath. It has been mentioned already that on the addition of copper this segregation is retarded mechanically, the dendritic copper alloy crystals, Cu_3Sn , forming a net work, which holds the antimony cuboids in place. The addition of copper increases the hardness, but also the brittleness of the ternary alloys in question.

The field VI-IV-V contains the alloys very rich in tin and comparatively pure in antimony and—eventually—lead. On cooling down this group of alloys, tin crystals, holding antimony in solid solution, are first solidified, the eutectic Pb Sn being formed as soon as the concentration of the melt has reached the line IX-IV.

Of the remaining fields, II-III-VIII is of little importance, the first crystals separating consisting of lead. The same is true of the alloys covered by field III-IV-IX.

Some of the most important cheap bearing alloys are found in field II-III-VIII, the Jacobi bearing metal composed of 85 per cent lead, 5 per cent tin, and 10 per cent antimony being the most prominent. Figure 7 indicates the position of some of the important lead-base bearing metals within the various fields of the diagram, the numbers employed representing the following alloys:

- | | |
|------------------------------|-----------------------------|
| 1. Italian Ry. | 8. Jacobi B.M. |
| 2. American Bearing (2% Cu) | 9. Graphite B.M. |
| 3. Hoyle's Alloy | 10. American Ry. B.M. |
| 4. American Bearing (1% Cu) | 11. Glyco-Turbo B.M. |
| 5. Submerged Bearing (2% Cu) | 12. Hughes B.M. |
| 6. Standard Antifriction | 13. French State Ry. |
| 7. Sperry's B.M. | 14. Guillet, Bearing P.L.M. |

TABLE 9.—SOLIDIFICATION INTERVALS OF TERNARY LEAD-BASE BEARING METALS

Composition, per Cent			Solidification, degrees C.	
Pb	Sn	Sb	Beginning	End
90.0	2.0	8.0	268	242
85.0	5.0	10.0	250	242
70.0	20.0	10.0	234	184
80.0	5.0	15.0	269	242
80.0	10.0	10.0	242	242
70.0	15.0	15.0	261	184
71.0	5.0	24.0	325	242
75.0	10.0	15.0	265	242
60.0	20.0	20.0	297	184
70.0	10.0	20.0	289	242
50.0	40.0	10.0	241	184

lead crystals separate out first, the antimony-lead compounds, representing the hard constituents of these binary alloys, forming the eutectic, which solidifies at 247° C. Lead-antimony alloys containing less antimony than the eutectic composition (13% Sb) consist of the eutectic surrounded by dark, primary crystallized lead crystals, while the alloys with higher antimony contents consist of the eutectic surrounded by bright antimony-crystals. Hardness and compressive strength of the alloys increase rapidly until the eutectic composition is reached, while on passing this point the respective increases are only slight. The alloys with up to 13 per cent antimony are plastic and rollable. With the appearance of primarily solidifying antimony crystals, there is a rapid increase of brittleness, so that at an antimony content of 25 per cent, the alloys cannot be rolled any more.

In modern lead-base bearing metals, part of the antimony or lead contents are replaced by tin, which increases the hardness and strength of the alloys without causing a corresponding increase of brittleness. The hardness of lead-antimony-tin alloys containing more than 30 per cent tin may be considerably increased by subsequent annealing of the rapidly cooled castings.

It is generally believed that in lead-base bearing metals the tin contents should not be much less than 10 per cent, with an antimony range of from 10 to 18 per cent for alloys containing from 10 to 25 per cent tin. However, the higher the tin contents, the more anti-

mony may be added without inducing excessive brittleness, and at a tin content of from 30 to 40 per cent, the antimony contents may be increased to about 25 per cent. Thus, a bearing used by the Italian Railroad and containing 37 per cent lead, 38 per cent tin and 25 per cent antimony is reported to have given excellent results.

Table 10 gives a list of well known lead-base bearing alloys mentioned in literature.

TABLE 10.—LEAD-BASE BEARING METALS

Purpose (Names)	Per Cent Pb	Per Cent Sn	Per Cent Sb	Per Cent Cu	Per Cent
Bearing.....	10.0	75.0	12.0	3.0	1.0 Zn
Bearing, Campbell.....	10.0	75.0	15.0		
Bearing, Campbell.....	11.8	74.0	9.5	4.7	
Marine Engines, Buchanan.....	17.0	77.0	3.0	3.0	
Marine Engines, Buchanan.....	25.5	61.0	10.5	2.8	
Roberts-Austen.....	33.0	53.0	10.6	2.4	
Italian Ry.....	37.0	38.0	25.0		
Bearing (American).....	40.0	42.0	16.0	2.0	
French State Ry.....	40.0	45.0	15.0		
French Eastern Ry.....	42.0	42.0	16.0		
Hoyle's Alloy.....	42.0	46.0	12.0		40 Zn
Kniess Bearing Metal.....	42.0	15.0		3.0	
Navy Bronze No. 4.....	44.0	36.0	16.0	4.0	
Bearing (American).....	46.0	36.5	16.5	1.0	
Submerged Bearings.....	48.0	40.0	10.0	2.0	
Standard Antifriction.....	50.0	40.0	10.0		
Sperry's B.M.....	50.0	35.0	15.0		
Lead Pump Bearing.....	52.0	35.0	8.0	5.0	
Railway Bearings.....	60.0	20.0	20.0		
Jacobi B.M.....	62.0	27.0	10.0		
B.M. in Sugar Mills.....	62.5	20.0	16.0	1.5	8.3 Bi
Graphite B.M.....	65.0	10.0	25.0		
Dynamo Bearing.....	66.7	25.0			
Graphite Bearing Metal.....	67.73	14.38	16.73		
Graphite Bearing Metal.....	68.0	15.0	17.0		
American Ry. B.M.....	68.0	21.0	11.0		
Glyco Turbo B.M.....	69.58	8.21	21.56		
Glyco Turbo B.M. Sugar Mills....	70.0	8.0	22.0		
Hughes B.M.....	76.0	14.0	10.0		
French State Ry.....	70.0	20.0	10.0		
Bearing P.L.M. Guillet.....	70.0	10.0	20.0		
English Ry. Car Bearing.....	70.0	15.0	15.0		

TABLE 10.—LEAD-BASE BEARING METALS, *Continued*

Purpose (Names)	Per Cent Pb	Per Cent Sn	Per Cent Sb	Per Cent Cu	Per Cent
Paris-Lyon Ry.....	70.0	10.0	20.0		
Jacana B.M.....	70.33	10.11	18.99		0.01 Bi
Normal White B.M.....	71.0	5.0	24.0		
Marine Babbitt.....	72.0	21.0	7.0		
Heavy Marine B.M.....	72.0	21.0	7.0		
French Northern Ry.....	73.0	12.0	15.0		
French Eastern Ry.....	73.0	12.0	15.0		
American Ry. B.....	73.5	8.0	18.5		
Glyco Moteurs B.....	74.1	11.71	14.02		
French Western Ry.....	76.0	14.0			10 Zn
French Southern Ry.....	76.0	14.0	10.0		
Paris-Lyon Ry.....	76.0	14.0	10.0		
Italian Ry.....	76.0	14.0	10.0		
Glievor Bearings.....	76.5	8.0	14.0		1.5 Fe
Magnolia High Speed Shafting....	76.5	8.0	15.0	0.5	
Glievo Metal B.....	76.7	7.86	14.02		1.52 Fe
Colesco B.M.....	77.0	8.0	14.0	1.0	
Magnolia, Somewhat Hard.....	77.0	6.0	17.0		
Katzenstein B.M.....	77.6	7.3	16.8	0.4	
Tandem B.M.....	77.7	5.9	16.8		
Magnolia.....	78.0	6.0	16.0		
Magnolia.....	78.0		21.0		1.0 Fe
Magnolia.....	78.3	3.9	17.8	0.4	
Magnolia.....	79.4		20.2		Tr. Fe
Magnolia (English).....	80.0	5.0	15.0		
Compagnie d'Est.....	80.0	12.0	8.0		
Magnolia, Ordinary.....	80.0	5.0	15.0		
Rumanian Ry.....	80.0	12.0	8.0		
French Southern Ry.....	80.0		20.0		
Paris-Lyon Ry.....	80.0		20.0		
French Eastern Ry.....	80.0	12.0	8.0		
French Eastern Ry.....	80.0		20.0		
Belgian Ry.....	80.0		20.0		
Magnolia B.M.....	80.0	10.0	10.0		
Glyco-like.....	80.5	4.5	14.5		
Soft B.M., Fairlie.....	80.65	11.4	7.53	0.42	
Campbell.....	82.0	2.0	16.0		
Campbell.....	83.3	8.3	8.3		
Jacobi B.M.....	85.0	5.0	10.0		
Heavy loads, Lake.....	87.0	6.0	7.0		
Russian Ry., Lake.....	90.0	2.0	8.0		

Comparative tests carried out by the Westinghouse Electric and Manufacturing Co. with three representative bearing metal alloys gave the following results:¹

Table 11 gives the composition of the alloys tested:

TABLE 11

Alloy No.	Per Cent Sb	Per Cent Cu	Per Cent Pb	Per Cent Sn
A	8.0	2.0		90.0
B	8.33	8.33		83.33
C	14.0		78.0	8.0

Of these three alloys, A and C proved to be equally hard at 95° Fahr. At higher temperatures, C was the hardest, the hardness of the alloys A and B showing but little difference. Pressure tests and actual running tests proved alloy C, rich in lead, to be superior to the others.

As a result of comprehensive mechanical and metallographical tests, the Westinghouse Co. offered the following suggestions concerning the casting and general treatment of white bearing metals.

1. It is good policy to use only one lead-base and one tin-base bearing alloy, which may then be perfected in accordance with the specific requirements.

2. Of greatest importance to the attainment of satisfactory bearing qualities is the careful choice and control of the raw materials employed, and only pure metals and alloys should be used for this purpose.

3. More important than the excessively exact composition of bearing metals are correct method of alloying, melting and casting. The metal should be alloyed at temperatures as far as possible below the melting temperature of the most refractory constituent, a temperature of about 930° Fahr. or less being sufficiently high for alloying good bearing metals. From the time of commencing fusion until complete solidification of the fused metal this should be kept protected by a charcoal cover.

4. The most favorable casting temperature is from 850 to 880° Fahr. Lower casting temperatures cause the formation of coarsely

¹ Iron Age, 1918, pp. 22, 8.

granular structures, while higher temperatures tend to increase the softness of the bearings.

5. Pre-heating the bearing at a temperature of 212 to 300° Fahr. insures the production of a uniform non-porous casting, and permits the metal to adhere to the shells, which partly shrinks along with the casting.

6. During and after pouring, until the casting is completely solidified, it is to be protected against impacts or other disturbances.

7. The bearing metal should contain as large a proportion of hard particles as possible, but these should not be in direct contact with each other. The soft matrix should be strong enough to hold the hard particles in place.

8. A Brinell hardness of No. 30 must be considered the most favorable in tin-base alloy, the corresponding degree of hardness of the lead-base alloys being 23.5 Brinell.

Lead-Copper-Antimony Alloys.—Another, but little known type of antifriction alloys, that is to say, lead-base bearing metals (which alone should be termed “antifriction metals”) are the lead-copper-antimony alloys, a few of which are given in Table 12.¹

TABLE 12.—LEAD-COPPER-ANTIMONY BEARING METALS.

No.	Per Cent Pb	Per Cent Cu	Per Cent Sb
1	66.6	12.9	20.5
2	66.6	23.2	10.2
3	80.0	7.75	12.25
4	80.0	13.9	6.1
5	90.0	3.8	6.2
6	90.0	6.9	3.1

The general characteristics of these alloys are similar to those of the other antifriction alloys. Copper and antimony form the hard compound SbCu_2 . Part of this crystallizes out in acicular form, while the rest goes into the eutectic. As a rule, these alloys should not contain more than 10 per cent copper and from 15 to 25 per cent antimony.

Zinc-Base Bearing Metals.—Alloys of zinc, tin and antimony, containing various percentages of copper, lead, and aluminum qualify

¹ E. F. Law, “Alloys,” p. 253.

as bearing metals almost exclusively by their high compressive strength, the other antifrictional properties being less satisfactory than those of any of the other correctly composed groups of bearing metals. They are therefore employed only for heavily loaded bearings where high compression strength, combined with cheapness, are the chief requirements. Table 13 gives the compressive strength of a number of straight zinc-antimony-tin alloys as determined by Charpy.

TABLE 13.—COMPRESSIVE STRENGTH OF ZINC-BASE BEARING METALS

Composition, per cent			Load corresponding to a compression of 0.2 mm. (kg.)	Load Corresponding to a compression of 7.5 mm. (kg.)
Zn	Sb	Sn		
100			500	4200
90	10		2450	Broke at 5000
80	20		3000	Broke at 4000
70	30		4100	Broke at 4700
90	5	5	1100	3950
80	10	10	1350	4150
70	15	15	1800	5200
80	5	15	1120	3550
70	7.5	22.5	1225	3500
60	10	30	1240	3350
90		10	750	3050
80		20	850	2725
70		30	850	2500
60		40	575	2175

The original zinc-base bearing metals are straight zinc-tin alloys, the addition of different amounts of copper, antimony, and lead being made to increase the useful hardness without causing a correspondingly large increase of brittleness.

Zinc-base bearing metals containing free zinc do not give satisfactory service due to the tendency of the zinc to adhere to the iron at comparatively low temperatures. Another grave disadvantage of these alloys is their higher degree of brittleness.

Table 14 gives a list of some of the zinc-base bearing metals mentioned in literature.

TABLE 14.—ZINC-BASE BEARING METALS

Purposes (Names)	Per cent Zn	Per cent Sn	Per cent Cu	Per cent Sb	Per cent Pb	Per cent
Russian Packing.....	98.5	0.98			0.32	0.16 Fe
Hamilton Metal.....	93.4		3.5	1.5	3.1	
For heavy work.....	90.0	1.5	7.0	1.5		
Leddel Alloy.....	90.0		5.0			5.0 Al
Russian State Ry.....	90.0	1.5	7.0	1.5		
Cheap Krupp Mill B.A...	90.0	1.5	7.0	1.5		
Ehrhard's Metal.....	89.0	4.0	4.0		3.0	
Bearings for Common Work (Hiorns).....	88.0	2.0	8.0	2.0		
Cheap Krupp Mills B.A...	88.0	2.0	8.0	2.0		
Leddel's "Aluminum Bear- ing".....	87.5		6.25			6.25 Al
Glyko Metal.....	85.5	5.0	2.4	4.7		2.0 Al
Salge Metal.....	85.5	9.9	4.0		1.1	
Ledebur's B.M.....	85.0		5.0	10.0		
Dunlevic & Jones Anti- friction.....	85.0		5.0	10.0		
Saxonia Metal.....	84.8	5.3	6.0		3.0	0.2 Al
Ehrhard's B.M.....	84.4	0.2	10.9		1.2	2.5 Al
Sulzer's Antifriction....	83.6	9.9	4.0		1.2	
Pierrot's B.M.....	83.3	7.6	2.3	3.8	3.0	
Iridium B.M.....	83.0	15.75	1.25	Tr.		
Germania B. Bronze.....	80.4	9.6	4.4		4.7	0.8 Fe
Fenton's B.M. (Schott)...	80.0	14.5	5.5			
F. Axle Boxes and Cars...						
Fenton's B.M.....	80.0	14.0	6.0			
Fenton's B.M. II.....	80.0		5.5	14.5		
Dunlevic & Jones.....	80.0		8.0	10.0		
"English" B.M.....	80.0	14.5	5.5			
Iridium II.....	77.25	21.63	1.12	Tr.		
Ledebur's B.M.....	77.0	17.5	5.5			
Krupp Mills II.....	76.92			7.70	15.38	
Becker's Alloy for rapidly revolving shafts.....	76.14	17.47	5.60			
Russian B.M.....	76.14	17.47	5.60			
English B.M. for heavy loads.....	76.14	17.47	5.60			
Glievor Metal.....	73.50	6.9	4.3	8.9	4.9	1.4 Cd
English Babbitt.....	69.0	19.0	4.0	3.0	5.0	
For Propeller Bushings...	69.0	26.0	5.0			
Tandem B.M.....	66.0	21.5	7.0		4.8	0.4 Al

TABLE 14.—ZINC-BASE BEARING METALS, *Continued*

Purposes (Names)	Per cent Zn	Per cent Sn	Per cent Cu	Per cent Sb	Per cent Pb	Per cent
Schomberg's B.M.....	59.4	39.9	0.38		0.21	0.15 Fe
"Aluminium B.M.".....	54.95	22.7	0.55		1.25	20.20 Al
Ry. Axles.....	52.0	46.0	1.6	0.4		
Dunlevic's B.M.....	52.0	46.0	1.6	0.4		
"German" B.M.....	50.0	25.0			25.0	
Kneiss B.M.....	50.0	25.0			25.0	
Automobile B.M. and sim- ilar purposes.....	47.5			5.0		47.5 Cd
Siemens & Halske.....	47.5			5.0		47.5 Cd
Wagner's B.M.....	47.0	38.0	1.0	6.0	4.0	
For heavy loads.....	47.0	38.0	1.0	6.0	4.0	
Krupp Mills I.....	45.5			9.0	45.5	
Kniess B.M.....	40.0	15.0	3.0		42.0	
For ordinary mills.....	40.0	15.0	3.0		42.0	
For propeller boxes.....	29.0	14.0	57.0			
Russian B.M.....	26.5	72.2	1.3			
Dunlevic & Jones Anti- friction.....	20.0			20.0	60.0	
Stephenson's Alloy.....	19.0	31.0	19.0			31.0 Fe

CHAPTER III

TYPE METALS

Not many years ago, when types were set up by hand, the matter of choice of type metals or printers' alloys was a comparatively simple consideration. The composition of the few different alloys used was only governed, as a rule, by the size and the style of types used, small and thin-lined type requiring fluid and tough alloys, while with larger and simpler types, fusibility and fluidity of the metals became of increasingly lesser importance. There can be no doubt, of course, that a considerable proportion of type setting is still being carried out by hand, but by far the greatest volume of work is now handled by mechanical type-setting devices, such as the linotype, typograph and monotype machines.

It is evident that since, apart from the general properties of type metals, the printing alloys used in the machines must be suited to the complicated mechanism of the type-setting apparatus, the requirements are correspondingly higher, although from the point of economy, modern printing machines are superior in that for many of the ordinary purposes, alloys containing comparatively small percentages of tin give satisfactory results, if the other requirements such as fusibility, fluidity, freedom from impurities and satisfactory metallurgical properties are fulfilled.

A short description of the mechanism and operation of the various types of modern printing machines will assist in understanding the important points at issue.

The *Linotype* machine, developed into a practical type-setting mechanism by Ottmar Mergenthaler of Baltimore, represents a very ingenious and complicated piece of machinery. Operated by one man, who works a keyboard similar to that of a typewriter, it assembles the matrices corresponding to the types of a full line, casts the "slugs," and, after cutting and trimming the castings, ejects and assembles them in the correct order for printing. The matrices, with the characters on one edge, are assembled in a magazine, and are

discharged by gates, operated from the keyboard, being transported to the assembler block, where they are set up in the proper order and pressed together so as to form a compact line. A lever, operated by the compositor causes this line to be moved opposite the mouth of the mold, when a jet of molten type metal is injected into the mold, thus casting a slug, which represents one line of type faces. This is trimmed by sharp knives, ejected from the mold and placed in position ready for the form.

The *Typograph*, *Intertype*, and similar machines are similar to the linotype in principle, the chief differences from the metallurgical point of view being found in the size and shape of the apertures of the mold, which usually permits of the use of harder type metals.

The *Monotype* machine operates on an entirely different principle. It consists of two separate members, a ribbon punching machine operated from a large keyboard, and a composing and type casting mechanism. The keyboard is made up of about 260 keys, representing all the characters required while a number of keys operate several parts of the composing machine. The operation of the keys causes the machine to perforate a strip of paper by means of pneumatically operated punches. The perforations, standing in a transverse line across the paper band, stand for the various words, and their relative position in the line for the letters composing the words. This paper band runs up into a spool which is then transferred to the composing and casting machine, where it is made to pass over the edge of a tracker board containing a number of holes corresponding to those which have been punched into the paper band. Whenever one of these perforations coincides with the proper hole in the tracker board, a jet of compressed air passes to the mechanical device operating the matrix carrier, which brings the appropriate matrix into position. This is then moved in position opposite to the mold and the single letter is cast. The individual letters are automatically placed in proper order.

The *Stereotype* process represents the most modern development of the printing art which enables the printer to produce as many replicas of each form as required without setting up duplicate forms of type, thus permitting the simultaneous operation of a number of printing machines by using the several replicas of one form. The principle of this is the following:

A sheet of of papier-maché, termed flong, is moistened and laid over the type form, into which is pressed by means of a molding

press. After drying, the flong is fastened in a casting mold, into which is cast the stereotype metal. If the plate is to be used for rotary printing, it is cast in the form of a half cylinder, two of them being placed together to cover the printing machine cylinder.

Electrotyping may be considered a variation of the stereotype process which, while slower, yields a considerably larger number of sharp impressions than stereotypes. It is obvious that on making a number of castings from the papier-maché matrices, the sharpness of the characters is bound to suffer. The process is carried out as follows:

A plate, consisting of a molding composition rich in wax is brushed over with black lead, a conductor of electricity, and polished. While still warm, the form is impressed upon its surface, which is *x* subjected to a "building-up" process by dropping molten wax upon those places which are to appear white in the print. After being covered with another film of black lead, the plate is immersed in the electrotyping bath, where copper is deposited on the surface in a sufficiently strong layer to form the "shell." This is backed with type metal, and trimmed and planned. As in stereotyping, semi-cylindrical plates may also be produced for use in rotary presses.

Properties of Type Metals.—The essential general requirements of good type metals are:

1. The metal must give good, sharp castings.
2. It must be sufficiently strong to withstand the mechanical wear and the pressure imposed without losing its form.
3. The alloy must not dross during melting and type setting.
4. It must remain free from solid impurities at all times.
5. The melting—or freezing—temperatures should be sufficiently low to keep the metal thoroughly fluid during casting.
6. The alloy should have a small freezing range, that is, as small a period of solidification as possible since the various operations of the type-setting machines—casting, trimming, and ejection—follow each other in rapid succession.

The first requirement is fulfilled by plain lead-antimony alloys containing not more than 15 per cent of antimony, which possesses the property of expanding on cooling. However, since these alloys are of a vitreous structure, they are not strong enough to withstand hard wear, and not sufficiently resistant against the scouring action of the caustics, more or less tin is added, which by forming hard crystals, SnSb, introduce the necessary hardness and compressive

strength without deteriorating the other properties required in type metals.

The tin contents of the common type metals ranges from 3.5 to 9 or 10 per cent, best results being obtained with percentages of from 6 to 8 per cent. Richer alloys should only be used for special purposes.

The general properties of the various groups of type metals, as implied by the characteristic requirements of the respective processes may be summed up as follows:

1. Since the *Monotype* forms are made up of single types, thus lacking the mass support of the others, monotype metal must be stronger and harder than any other of the type metals used in modern printing work, the general properties and composition resembling those of common type metals used for hand-set types. However, since on casting the small bulk of the individual types solidifies rapidly, sufficiently larger percentages of tin and antimony may be added to supply the mechanical requirements and to produce an extremely fine and sharply drawn face.

2. *Linotype* metal, being cast into long slugs, may be made appreciably softer and weaker than the monotype alloys, a tin content of 3.5 to 5 per cent and an antimony content of from 11 to 13 per cent giving satisfactory service.

3. While in view of the considerable mass support characterizing the *Stereotype* plates, the strength requirements for similar work are less exacting than for monotype and linotype metals, these plates are in the majority of cases employed in newspaper printing, where many thousands impressions are usually taken from one plate within one or two hours. Since the semi-cylindrical plates used in rotary printing presses are subjected not only to compressive stresses but to a strong abrasive action as well, the metal must be both strong and tenacious, the percentage of tin and antimony required being correspondingly high. For less exacting service, where flat stereotype plates are used, the tin and antimony contents need not be as high, the average figures ranging from 3.2 to 5 per cent tin and from 13 to 18 per cent antimony. The freezing temperatures should be comparatively low and the freezing range as small as possible. In modern pressure-cast machines the metal is actually introduced into the mold in a state of incipient solidification in order to shorten the period of solidification.

Table 15 gives the composition of type metals mentioned in literature.

TABLE 15.—TYPE METALS

Purposes (Names)	Per cent Sn	Per cent Sb	Per cent Pb	Per cent of other elements
<i>Type Metal</i>	6.0	16.0	78.0	
Type Metal.....	6.5	16.0	77.5	
English Type metal.....	6.5	16.0	77.5	
English Type metal.....	9.1	19.5	69.2	1.70 Cu
Common Type Metal.....	10.0	30.0	60.0	
Common Type Metal.....	10.0	18.0	70.0	2.00 Cu
German Type Metal.....	11.90	17.85	59.54	4.76 Cu 1.19 Bi
English Type Metal.....	12.0	24.0	63.2	0.8 Cu
English Type Metal.....	14.5	24.2	60.5	0.8 Cu
English Type Metal.....	15.0	26.0	58.0	1.0 Cu
German Type Metal.....	15.0	25.0	60.0	
French Type Metal.....	15.0	30.0	55.0	
Small Types.....	20.0	16.0	64.0	
German Type Metal.....	20.2	18.8	61.3	
French Type Metal.....	22.0	23.0	55.0	
French Type Metal.....	22.1	22.7	55.0	
Best Type Metal.....	25.0	25.0	50.0	
Standard Type Metal.....	26.0	15.0	58.0	1.00 Cu
German Type Metal.....	34.6	5.4	60.0	
German Type Metal.....	35.0	5.0	60.0	
Common Type Metal.....	40.0	4.5	55.5	
German Type Metal.....		15.39	76.92	7.69 Bi
Small Types.....		15.40	69.3	15.4 Bi
Small Types.....		15.40	77.0	7.60 Bi
Small Types.....		16.75	83.25	
Small Types.....		25.0	75.0	
<i>Standard Linotype</i>	5.0	12.0	83.0	
English Linotype.....	3.0	12.0	85.0	
Cheap Linotype.....	3.5	11.0	85.0	
Ordinary Linotype.....	5.0	13.0	82.0	
English Linotype.....	5.0	12.0	83.0	
English Linotype.....	6.0	12.0	82.0	
<i>Monotype</i> (Standard).....	8.0	18.0	74.0	
Ordinary <i>Stereotype</i>	3.2	14.8	82.0	
Ordinary <i>Stereotype</i>	4.0	20.0	76.0	
Standard <i>Stereotype</i>	4.5	13.0	82.5	
English <i>Stereotype</i>	6.0	12.0	82.0	
English <i>Stereotype</i>	7.0	23.0	70.0	
English <i>Stereotype</i>	17.0	16.0	67.0	

TABLE 15.—TYPE METALS, *Continued*

Purposes (Names)	Per cent Sn	Per cent Sb	Per cent Pb	Per cent of other elements
English Stereotype.....	20.0	16.0	64.0	
English Stereotype.....	60.0	5.0	35.0	
English Stereotype.....		15.4	69.3	15.4 Bi
English Stereotype.....		15.4	77.0	7.6 Bi
English Stereotype.....		16.75	83.25	
English Stereotype.....		25.00	75.00	
<i>Electrotype (Standard)</i>	3.0	4.0	93.0	
Note Printing Metal.....	10.0	30.0	60.0	
Note Printing Metal.....	10.0	18.0	70.0	2.00 Cu
Note Printing Metal.....	15.0	33.0	50.0	
Note Printing Metal.....	20.0	20.0	60.0	
Note Printing Metal.....	20.0	25.0	55.0	
German Printing Metal.....	34.6	5.4	60.0	
German Printing Metal.....	35.0	5.0	60.0	
German Printing Metal.....	40.0	4.5	55.5	
German Printing Metal.....		9.1	90.9	
German Printing Metal.....		25.0	75.0	
Plates for Engraving Music.....	12.0	8.0	64.0	16.0 Zn
Plates for Engraving Music.....	37.5	2.5	60.0	
Plates for Engraving Music.....	50.0	50.0		
Plates for Engraving Music.....	75.0	25.0		
<i>Clichier Metal</i>	18.18		27.27	54.55 Bi
Clichier Metal.....	18.75		31.25	50.0 Bi
Clichier Metal.....	18.75	12.5	31.25	37.50 Bi
Clichier Metal.....	21.05	15.8	21.05	42.10 Bi
Clichier Metal.....	21.43		50.0	28.57 Bi
Clichier Metal.....	22.22		22.22	55.56 Bi
Clichier Metal.....	26.0		50.0	22.5 Cd
Clichier Metal.....	33.0		46.0	21.0 Cd
Clichier Metal.....	36.0		50.0	14.0 Cd
Clichier Metal.....	48.0	10.5	32.5	9.0 Bi
Clichier Metal.....	80.0		5.0	15.0 Bi

In remelting type material, all "line cuts" and brass strips, which may have dropped into the type scrap, must be removed before melting the scrap, since these will introduce zinc into the alloy. The removal of zinc is effected by steaming as described on page 134.

After repeated remelting, the tin contents of type metals are gradually lowered, a standard 5 per cent linotype alloy gradually

being converted into a cheap linotype material. The apparently common opinion held by type metal manufacturers that the comparatively large percentage of tin found in tin ashes, and the corresponding impoverishment of the metal in tin, is due to the settling of the heavier lead constituent at the bottom and to a proportionate increase of the tin contents of the top layers, is erroneous of course. This is best demonstrated by the fact that the tin contents of the ashes will always be found to be higher than even those of the top-layer of the metal. The true reason for the concentration of tin in the ashes is based on the various susceptibilities of the different constituents of the alloys to oxidation. Under the conditions obtaining, tin is the first metal to be oxidized, antimony second, and the bulk of the lead last. On account of the preponderating percentage of lead present, the ashes contain a relatively small amount of tin, but this percentage is still considerably higher than that of the tin present in the alloy.

Influence of Impurities in Type Metals.—The most common impurities found in white metals generally are: copper, zinc, iron, sulphur, and arsenic, of which the last four are absolutely deleterious to the properties of type metals.

Zinc, tending to form infusible mixtures with tin, antimony and, especially, copper, causes drossing which disqualifies the metal for use in type-setting apparatus.

Arsenic, if present in small quantities, causes brittleness of the alloys and lowers the tenacity and compressive strength of the matrix. Attention is called to the fact, however, that many of the earlier type metals show considerable percentages of arsenic. Table 16, at top of next page, gives the composition of some alloys of this type as determined by Meyer and Schuster:¹

Iron, entering the hard particles, increases the tarnishing tendencies of the types, while *Sulphur* induces tarnishing to a much higher extent than iron. Sulphur also gives rise to the formation of drosses.

While if present in quantities of one or a few tenths per cent, *Copper* is usually considered a deteriorating impurity, it is sometimes added intentionally to ordinary type metals to increase the hardness of the types. In view of the difficulties connected with the treatment of these alloys and on account of the tendency of the hard constituents to separate out, copper is not added to linotype, mono-

¹ Zeitschrift für Anorganische Chemie, 1914, 121.

TABLE 16

Composition, per cent				Condition of the types after long periods of storage
Pb	Sb	Sn	As	
70.18	22.87	6.00	0.23	Good.
78.56	19.97	0.12	0.48	Strongly corroded.
69.49	23.29	6.04	0.14	Good.
77.02	22.49		0.13	Strongly corroded.
79.41	18.76	0.65	0.20	Good (60 years old).
81.60	17.93		0.09	Good (75 years old).
82.79	16.71		0.08	Good (75 years old).
72.70	21.55	5.55	0.13	Good.
71.92	22.01	6.28	0.16	Good.
76.77	22.43	0.80	0.20	Good (40 years old).

type, electrotpe and other alloys used in modern mechanical type-setting apparatus.

A few per cent of bismuth are often added to type metals used for the casting of small types in order to improve the fusibility and fluidity of the metal. Where more than a few tenths of a per cent of this element are added, it replaces the tin, so that to all intents and purposes a new group of alloys, the lead-antimony-bismuth alloys, is formed.

Type metals free from impurities and containing the required percentages of elements do not give rise to difficulties unless incorrectly treated. This is particularly true of surface oxidation, or tarnishing, which, dark gray of color, often penetrates deeply into the metal, causing the gradual destruction of the types. Microscopic examination of a number of old type metals made by Meyer and Schuster¹ showed that in all the cases under observation this phenomenon had not been caused by the chemical composition of the types, but by incorrect casting and faulty methods of cleaning and storing. Zinberg found that the durability of types is governed by the amount of lead contained. The higher the lead contents the less resistant are the types to the oxidizing influence of moisture.

¹ Zeitschrift für Anorganische Chemie, 1914, p. 121.

CHAPTER IV

SOFT SOLDERS

"Soldering" is the term applied to the joining of heated solid metals and alloys by means of alloys consisting of two or more metals having a melting point lower than those of the joined metals, and applied by filling a joint or covering a juncture. The alloys used for this purpose are termed "solders."

In spite of their eminent importance and wide application in the industries and trades, the scientific study of solders and of the principles underlying the choice of solders and of correct soldering methods has been very much neglected. And this attitude of scientists and research workers appears to be strongly reflected upon the views and customs of the trade.

It is a well known experience of the producers of solder alloys that excellent and technically valuable alloys are frequently refused by the trade because of the lack of some unimportant and totally superficial property specified by the consumer, so that the producers of such alloys are often forced to supply the solder with certain metallic additions which, while conferring the properties demanded, are not always favorable to the mechanical and chemical properties required in perfect solder alloys.

Determined efforts on the part of the metallurgical industries to reduce the costs of the alloys and to evaluate the technical advances effected in science and engineering by improving and simplifying the composition of the alloys and replacing the expensive components, such as tin, by cheaper metals, without at the same time lowering the quality and their suitability for their respective purposes, are usually meeting with the determined resistance of the small trade, which prefers to abide by the old and tried-out compositions, and to judge the value of solder alloys by phenomena such as color, sound and other "practical" indications.

For instance, while the usefulness of the soft solders is exclusively governed by their composition, the trade and the small indus-

tries are mainly concerned, as a rule, about the favorable appearance of the solder strips, which, as is well known to every metallurgist, may be influenced one way or the other by a number of factors and tricks without in any way indicating the suitability of the alloys for the purposes in question. This is best illustrated by the fact that the same appearance of the solder strips and absolutely similar "practical" reactions may be imparted to a large number of alloys differing not only in the percentage of tin contained but containing numerous other elements intentionally and unintentionally added, which may influence the general mechanical and the soldering properties in more than one way. The following table gives a list of factors, each of which influences the appearance of solder strips:

1. The composition of the alloy,
2. The impurities contained,
3. The methods of production and refining employed,
4. The pouring temperatures of the alloys,
5. Thickness and length of strips,
6. Temperature of the mold,
7. Material composing the mold.

Necessary Properties of Soft Solders.—A high grade white metal solder should possess the following essential properties:

1. The melting point of the solder must be sufficiently low to permit its use without endangering the mechanical properties of the soldered bodies by overheating. It should not be too low, however, in order to avoid softening of the solder if the soldered metal is occasionally heated a little above the usual temperatures. The composition of the solder must therefore be governed not only by the nature and properties of the base metal but also by the thermic treatment to which this may be exposed later on.

The smaller the difference between the melting points of the solder and the soldered metal, the stronger the joints, while if the melting point of the solder is considerably lower, the strength of the joint is only governed by the adhesive force of the solder but not by its intrinsic strength.

2. The various solders should be composed so as to enable them to form alloys with the metal to be soldered, that is to say, to melt together with the base metal during the short time of fusion. In contrast to former theories, it is now recognized that the joining effect of the solders is not due to adhesion, but to diffusion of the

solder and the soldered material into each other. All components, therefore, that favor the alloying of the soldered alloys with the base metal are strictly advantageous if the interaction of the two alloys or metals does not deteriorate the mechanical properties of the solder. It will be shown that in very many instances these properties of white metal solders may easily be obtained with alloys much poorer in tin than is ordinarily thought possible, or by using considerable percentages of relatively cheap substitute metals such as cadmium.

3. Adhesion of the solder to the base metals must be perfect.

4. The mechanical properties of the soldered joints in the cold state, particularly the strength, hardness and tenacity, must correspond to the respective properties of the soldered metals.

5. The solder alloy as well as the lines of contact between solder and soldered metal must not induce corrosion, or be less resistant against all common corrosion agencies than the soldered metals.

6. At the soldering temperatures applied the solders must be sufficiently fluid to fill up the joints, without, however, "running away" at the temperature of the soldering tool.

7. For certain decorative purposes the color of the solder must correspond closely with that of the base metal.

Considering their tin contents, the soft solders of the tin-lead group are usually divided into three types of alloys, namely, (1) the common solders, containing more lead than tin, (2) medium solders, containing equal parts of lead and tin, and (3) best solders, containing more tin than lead.

The most widely used type of common solders are the Plumbers' solders containing from 29 to 41 per cent of tin. Of these, the alloys with 29 to about 33 per cent of tin represent typical "wiping solders," being used for wiping joints of lead pipe and lead plates. This property is derived from the fact that the range of solidification of these alloys is comparatively wide, amounting to about 160° Fahr. in the case of lead-tin alloys containing from 30 to 32 per cent tin. In passing from the liquid to the solid state, these alloys assume a pasty condition, consisting as they do of a mixture of solidified crystals of lead and liquid eutectic, and during this period they may be spread, wiped, or smeared onto any object to which they adhere when cold. For lead cables or similar work, the wiping solder should carry a little more tin, the average tin contents of alloys of this type ranging from 34 to 37 per cent.

Soft solder containing in the neighborhood of 25 per cent tin does not work well with the soldering tool, but must be applied with the flame. For construction work and ordinary plumbing purposes the tin contents need not be higher than 35 per cent, although, as a rule, solders with from 35 to 40 per cent tin are employed for this work. For zinc sheets and galvanized sheets, the tin contents of the solders generally used are also higher than necessary, alloys containing from 33 to 35 per cent tin giving excellent service for all ordinary work of this type. Timed electrical joints, tin-plated material in general, and brass articles require a solder containing from 40 to 42 per cent tin, while high grade material of this type such as brass and tin plate articles used in electric meters require 50 per cent solders, that is, such containing equal parts of lead and tin. The same quality of solder is usually employed for fine tin-smith's and coppersmith's work, as well as for high grade galvanized articles.

For ordinary work requiring low melting points such as delicate steel articles in electric apparatus, steel tube joints, and for articles composed of metals and alloys of comparatively low melting points a solder containing 60 to 65 per cent tin should be employed, while for sanitary apparatus and other work requiring sanitary considerations, solders containing at least 85 to 90 per cent are used.

Table 17 gives the composition of lead-tin solders mentioned in literature.

The three more or less common impurities, which may be introduced into the alloys by the raw materials used in their production, are zinc, arsenic and copper. Antimony may also be mentioned in this connection, although this is often added intentionally in amounts of up to 2 per cent.

Zinc, even in traces, disqualifies any white metal alloy for use as solders since as low a percentage as 0.01 per cent causes the formation of a film of oxide which, apart from spoiling the surface appearance of the solder, prevents the adhesion of the solder metal to the base metal, and causes the gradual deterioration of the mechanical properties chiefly required for solders such as tensile strength, ductility and tenacity. This fact is convincingly demonstrated by the gradual destruction of originally pure white metal solders used on zinc or zinc-plated articles if hydrochloric acid is used as a flux,

TABLE 17.—SOFT SOLDERS

Purposes (Names)	Per cent Sn	Per cent Sb	Per cent Pb	Per cent Bi	Degrees F.
Cheap, fusible.....	3.7	7.9	R.		457
Suitable for iron.....	6.9	9.8	R.		453
Kupper's Patent Solder.....	6.9	9.8	R.		453
Kupper's Patent Solder.....	7.0	9.5	R.		450
	15.0	7.0	R.		457
For tin-plated sheets and brass....	15.0	7.0	R.		457
Kupper's Patent Solder.....	15.0	7.0	R.		457
	15.5	7.0	R.		457
Flame soldering, not suitable for soldering with iron (German Standard Spec.).....	25.0		R.		482
American Solder, coarse.....	25.0		R.		482
Construction and Common Solder- ing (German Standard Spec.)...	30.0		R.		481
Dipping baths (British Standard)...	29-31	0.0-0.3	R.		
Plumber's Solder (British).....	30.5	1.5	R.		
Zinc sheets and zinc plated sheets (German Standard Spec.).....	33.0		R.		439
	33.3		R.		438
Lead Cable Wiped joints (Brit.)...	34-36	0.0-0.4	R.		
General Plumber's solder.....	39-41		R.		428
Tinned electrical joints, zinc and galvanized material.....	41-43	0.0-0.4	R.		
Brasses and Tinplate, etc.....	41.0		R.		
Tinsmith and coppersmith fine work soldering. General elec- trical work (British Standard)...	49-51	2.5-3.0	R.		395
Tinman's Solder.....	50.0		R.		390
Brasses and tin plate soldering in the electrical industries.....					
Closing of tin cans.....	50.0		R.		390
Fusible metal articles. Fine elec- trical work.....	60.0		R.		368
Eutectic Alloy.....	63.0		R.		359
Work requiring low melting points, steel tube joints (Brit. Standard).	64-66	0.0-1.0	R.		
Slicker Solder.....	66.0		R.		360
Special sanitary soldering.....	90.0		R.		419

which will cause gradual absorption of small quantities of zinc by the solder, increasing the brittleness to such a degree that a short time after application the solder commences to crumble.

White metal solder containing small amounts of zinc flows sluggishly under the soldering tool, and the lack of tenacity and ductility induced renders the solder extremely sensitive towards all bending stresses. Where bending stresses, etc., are non-existent, as for instance, in welding castings and other rigid articles, zinc will cause the gradual destruction of the solder and of the base metals at the line of contact by the lowered resistance of zincish alloys towards atmospheric corrosion.

It is sometimes claimed in technical literature that small additions of zinc to white metal solders will prove valuable in soldering brasses, galvanized iron, or other materials containing, or covered by, zinc, but such solder alloys have never been of practical value, and numerous experiments carried out by the author have shown that in all cases examined the presence of zinc was undesirable. These remarks do not pertain to straight zinc solders, of course, which are successfully employed in soldering aluminum and aluminum alloys, and in which zinc represents the chief constituent. (See page 90.)

Appreciable percentages of copper spoil the appearance of the soldering and decrease its resistance against atmospheric corrosion. Unless present in larger amounts, copper does not, however, deteriorate the mechanical properties of the solder. Since in the metallurgical production of solder alloys from secondary metals the removal of excessively high copper contents is very simple, taking place almost automatically with correct smelting and alloying processes, the solders contain comparatively small percentages of this element, which do not appreciably influence the soldering qualities of the alloys.

Relatively high copper contents are recommended for solders employed for soldering zinc and zinc-plated materials, since the latter are able to dissolve up to 3 per cent copper, thus increasing the rate of diffusion, which, as explained above, represent one of the chief factors in successful soldering.

Arsenic forms an all-around deteriorating constituent of solder alloys, although for purposes not requiring a high degree of ductility and tenacity arsenic is sometimes permitted in quantities of up to 0.05 per cent. Generally speaking, arsenic deteriorates the mechanical

properties of white metal solders such as ductility, tensile strength and, particularly, the adhesive force. The resistance of solders against atmospheric corrosion also is considerably reduced.

Opinions concerning the influence of *Antimony* in white metal solders are all but uniform, but it should be pointed out here that, disregarding the looks of the strips, the general prejudice entertained against the influence of certain small percentages of antimony in white metal solders by a majority of American users appears to be strongly exaggerated. While the presence of antimony may have a tendency of slightly decreasing the fluidity of solders, it is an established fact that the joints produced by solders containing correct percentages of antimony are considerably stronger and more resistant than those effected with the corresponding straight tin-lead alloys. According to several British investigators, the presence of antimony in solders lowers the resistance of these alloys against atmospheric corrosion as well as their adhesion to galvanized surfaces, but little of this kind of trouble has actually been experienced where the percentages of the antimony present did not exceed a reasonable limit. The adverse opinion of some British authors to these antimony contents appears to be justified by the unfavorable atmospheric conditions prevailing in certain sections of the British Isles.

The other disadvantages often charged to the presence of antimony, such as a pronounced decrease of fluidity, sluggishness under the soldering tool, unfavorable appearance, etc., are also valid only if excessive percentages of antimony are present in the solder. In addition to the disadvantages enumerated, high antimony contents tend to increase the brittleness and to lower the respective elongation values of the white metal solder. The permissible maximum percentages of antimony vary from 0.30 to 2.50 per cent, and are determined by the tin contents of the solder and the purposes for which the solder is to be used. For tinsmith's and coppersmith's solder, or for any other solder alloys not required to withstand high bending stresses, this percentage may even be increased to 3 per cent, while for soldering lead, lead-plated sheets and black iron sheets, solder containing from 7 to 9 per cent antimony is frequently being used in Europe. These alloys give very good results for a number of other purposes also. The British Engineering Standards Association in their report, No. 219, gave the following analyses of the usual grades of solder:

TABLE 18.—BRITISH STANDARD SOLDER

	Per cent Sn	Per cent Sb	Per cent Pb
1. Work requiring low melting points. Steel tube joints.....	64-66	0.0-1.0	Best
2. Tinsmith's and Coppersmith's fine working solder.....	49-51	2.5-3.0	Best
3. For general work.....	39-41	2.0-2.4	Best
4. Plumber's wiped joints.....	29-31	0.7-1.0	Best
5. General electrical purposes. Zinc and galvanized iron work.....	49-51	0.0-0.4	Best
6. Special electrical purposes.....	94-96	0.0-0.4	Best
7. Tinned electrical joints. Zinc and galvanized iron work.....	41-43	0.0-0.4	Best
8. Lead cable wiped joints.....	34-36	0.0-0.3	Best
9. For dipping baths.....	29-31	0.0-0.3	Best

Alloys containing still higher percentages of antimony are given in Table 19.

The Standard Specifications for Soft Solders adopted by the German Society of Engineers require that "since Tin-alloy is usually employed in the production of soft solders," the antimony contents of white metal solders must not exceed a proportion of 3.6% Sb:54.5% Sn. If lower antimony contents are desired, this is to be definitely stated.

TABLE 19.—SOFT SOLDERS RICH IN ANTIMONY

Number	Per cent Sb	Per cent Sn	Per cent Pb	Melting point, Degrees F.
1	7.5	3.7	88.8	457
2	9.8	6.9	83.3	453
3	7.0	15.5	77.5	457
4	7.0	15.0	78.0	457
5	9.5	7.0	83.5	453
6	7.0	4.0	89.0	451

The presence of antimony in the solder is an important factor in determining the appearance of the strips, a fact particularly significant in illustrating the radical difference between general views

concerning the influence of this element held by the trades and actual conditions. While in the opinion of the trade, the good appearance of a strip of solder is sufficient proof against the presence of appreciable quantities of antimony, actual conditions are such that in the case of all solders containing 50 per cent and less of tin, the appearance of solder strips is usually improved by the addition of from 1.5 to 2.0 per cent of antimony. Straight tin-lead alloys exhibit a perfectly bright and smooth surface only if the percentage of tin exceeds 49 or 50 per cent, while with 47 to 48 per cent tin much of this fair appearance is lost. However, if such alloys containing from 43 to 48 per cent tin hold about 2 per cent of antimony, their appearance is as good as that exhibited by a straight 50/50 solder.

Influence of Casting on the Appearance of Soft Solder Strips.—

The more gradual the rate of cooling, that is to say, the less rapid the solidification of the alloys, the more favorable the appearance of the surface of the strips. Any mold material therefore, possessing a low conductivity of heat is preferable to the iron and steel molds usually employed for this purpose.

Best results are obtained with strip molds made of hard marble. The plates are laid in an iron frame and may be made 20 inches long, the clearance between the strips being about 1 inch, that between the two extreme strips and the sides, about 1½ inches.

Any other influence decreasing the speed of cooling also improves the appearance of the strips. The molds should be prewarmed by returning the first set of strips to the melting pot. The more perfectly tempered the mold and the hotter the pouring temperatures, the better the results, although the pouring temperatures should not exceed a certain maximum determined by the composition of the alloys in order to avoid a "burned" appearance.

The size of the strips, that is to say, the volume of the metal composing a strip, also influences the appearance of the solder strips. The heavier the strips the better their appearance, a fact also due, of course, to the correspondingly lower rate of cooling.

The appearance of solder strips may be improved considerably by adding a little rosin or grease to the metal in the ladle previous to pouring.

Production of Powdered Soft Solder.—If it is desired to produce small quantities of powdered soft solder without procuring the machinery required for the manufacture of this article, the following method will give satisfactory results:

A ladle filled with the metal is taken from the melting pot and is left to cool until the alloy becomes pasty, stirring the metal constantly with a wooden stick. It is then quickly emptied into a strong linen bag, the upper part of which is twisted around until the metal fits tightly into the bottom section. If the metal is now beaten with a wooden hammer with smart quick taps, turning the bag constantly, it will fall apart and become a gritty powder within a few minutes. Best results are obtained with hard-wood hammers.

If the metal is poured into the bags at the right moment, that is, a few moments before complete solidification, or, in other words at the temperature of incipient solidification, the bags will not be damaged considerably and may be used a large number of times. The powder produced will be rather white, while with too high a pouring temperature the powdered solder becomes dark, or even black, from the carbonized particles of the bag.

Hammering should be continued until the metal feels only warm to the hands since the tin alloys are not only brittle while passing from the fluid into the solid state, but also at temperatures of from 320 to 480° Fahr., depending on the composition of the alloys.

Cadmium Solders.—On account of the practically complete isolation of the Central European countries from the international tin markets during the World War and their inability to obtain the quantities of tin required, it became necessary in these countries to develop a substitute alloy containing only metals produced within their own borders. The most important of the solder alloys thus developed were found to be the cadmium solders. The success achieved with many alloys of this type caused them to be retained for a number of purposes after the close of the war, particularly since the suitability of cadmium as substitute of tin is accompanied by a comparatively low price. Numerous experiments carried out by the author and many authorities have shown that the mechanical and chemical properties of lead-tin-cadmium alloys or even straight lead-cadmium alloys, if properly alloyed and applied, are not inferior to the corresponding straight tin-lead alloys, the only practical disadvantages being the somewhat darker color and, according to unproved English statements, a slightly lower resistance against atmospheric corrosion. If the solder alloy contains a few per cent of tin, corrosion of cadmium alloys by atmospheric influences is reduced to negligible proportions in any case.

In spite of these facts, and the much greater cheapness of cad-

mium solders, these alloys are still being regarded with suspicion by a large portion of the industries and trades, although appreciable quantities of these solders, containing varying percentages of tin and cadmium, are now being sold in this country.

The unfavorable attitude of part of the trade towards cadmium solders is actuated by the following more or less real disadvantages:

1. The slightly darker color of the seam, if compared to a straight tin-lead solder of high tin contents.

2. Since cadmium begins to oxidize about 30 to 50° C. (55 to 90° Fahr.) above the melting point of the cadmium solders, depending upon the composition of the alloys, it is necessary to maintain evenly low temperatures in melting and applying these solders.

3. Cadmium solders cannot be used with the fluxes generally employed for ordinary solders. According to N. F. Budgen,¹ glycerine will give fair results, the most satisfactory flux appearing to be the following mixture of fused chlorides:

Sodium chloride.....	11%
Potassium chloride.....	14%
Zinc chloride.....	65%
Ammonium chloride.....	10%

This flux may be used sparingly either melted or in dilute aqueous solution, but cannot, according to Budgen, be employed for soldering complicated parts such as electric motors where it is impossible to remove all traces left in excess.

The alleged difference of color existing between tin and cadmium solders becomes apparent only if the cadmium solder is compared with tin solders containing more than 75 per cent tin, and is of practical importance merely in the case of decorative art work. For most other purposes, however, this objection should not exist, practical considerations such as tensile strength, tenacity, strength, fluidity, adhesive properties, and cheapness of the solder being of chief importance.

Opinions concerning the gradual blackening of straight cadmium-lead solders by atmospheric influences are very much divided. It is possible, of course, that with particularly unfavorable atmospheric conditions, such as prevail in some parts of England, cadmium solders may not stand up as well as tin-lead solders, but there can be no doubt that for all general conditions an alloy composed of 10 per cent

¹ Metal Industry, N. Y., 1928, pp. 104, 106.

cadmium, 10 per cent tin, and 80 per cent lead will prove as resistant against atmospheric influences as a 50/50 tin solder.

Besides tin, a small percentage of zinc is useful in increasing the resistance of cadmium solders against atmospheric corrosion as well as in improving the adhesive force of the solder alloys. It is interesting to note in this connection that in contrast to the ordinary white metal solders, the intrinsic qualities of true cadmium solders are not deteriorated by small amount of zinc, but that, if correctly composed, they are actually stronger than lead-cadmium-tin alloys, especially at elevated temperatures. According to Hill (Research Laboratory, Westinghouse Electric and Manufacturing Company) the following cadmium-lead-zinc alloy is superior to the cadmium-lead-tin mixture:

Lead	90.8%
Cadmium	7.8%
Zinc	1.4%

This and similar alloys are giving very good results where the base metals to be soldered contain zinc themselves, or even with electrical work, particularly, since they possess an appreciably higher electric conductivity than the lead-tin or lead-tin-antimony alloys used for this purpose.

Attention is called to the fact that since zinc is only slightly soluble in lead-cadmium alloys, larger amounts than from 1.5 to 3.0 per cent should not be added, the excess zinc forming a separate layer above the alloy.

Table 20 gives the composition of the most important cadmium-lead and cadmium-lead-tin compositions employed in Europe, and which, apart from their superior suitability for a number of purposes, are intended for economy of tin.

TABLE 20.—EUROPEAN CADMIUM SOLDERS

Number	Per cent Pb	Per cent Cd	Per cent Sn
1	83	17	
2	85	15	
3	90	10	
4	90	5	5
5	85	10	5
6	80	10	10

Other alloys rich in tin and cadmium and remarkable for their low melting points are the following:¹

TABLE 21.—CADMIUM SOLDERS RICH IN TIN

Number	Per cent Cd	Per cent Pb	Per cent Sn	Melting point, Degrees F.
1	8	33	79	280
2	25	15	70	270
3	25	50	50	300

A series of comprehensive experiments were carried out by Carl E. Swartz² to determine the properties of a number of alloys of the lead-tin-cadmium system with reference to the suitability of these alloys for use as solders. These tests showed that solders containing cadmium would make joints equal in strength to joints made with lead-tin solders and that the cadmium alloys were suitable in other respects for use as solders. Similar tests made with the same alloys, to which 1.5 to 2.0 per cent zinc had been added, showed that the addition of zinc in this proportion improved the alloys for this use. The investigation indicated the solders having compositions in the neighborhood of the ternary lead-tin-cadmium eutectic (32 per cent lead, 50 per cent tin, and 18 per cent cadmium) as being the best of the ternary alloys for most soldering work, though compositions varying from this may be more desirable for certain purposes.

Experiments to determine the influence of bismuth on lead-tin-cadmium solders, with a view to lowering the melting points of the alloys, showed that the presence of large amounts of bismuth made the alloys too brittle to be useful as solders for most purposes. For some special purposes, however, bismuth may be added in small quantities.

Aluminum Solders.—The soft solders generally used for aluminum and its alloys contain tin as a base, with different proportions of zinc, aluminum, copper, lead and cadmium, which are added to obtain the soldering properties best suited for the treatment of the innumerable aluminum compositions produced. The difficulty in soldering aluminum effectively is almost exclusively due to the affinity of

¹ N. F. Budgen, *Metal Industry*, N. Y., March, 1925, pp. 104–106.

² *Brass World*, March, 1928, pp. 74, 77.

aluminum and most of its alloys for oxygen, which causes an oxide film to form on the surface of aluminum upon exposure to air.

The basic principles underlying the use and application of aluminum solders are well stated in the Circular 78, dealing with Solders for Aluminum, published by the Bureau of Standards.

1. "All metals or combinations of metals used for aluminum soldering are electrolytically electropositive to aluminum. A soldered joint is therefore rapidly attacked when exposed to moisture and disintegrated. There is no solder for aluminum of which this is not true."

2. "Joints should therefore never be made by soldering unless they are to be protected against corrosion by a paint or varnish, or unless they are quite heavy, such as repairs in castings, where corrosion and disintegration of the joint near the exposed surface would be of little consequence."

3. "Solders are best applied without a flux or by using paraffin as a flux, after preliminary cleaning and tinning of the surfaces to be soldered. The composition of the solder may be varied within wide limits. It should consist of a tin base with addition of zinc or of both zinc and aluminum, the chief function of which is to produce a semifluid mixture within the range of soldering temperatures."

Following are the suggested ranges of composition.

Tin-Zinc solders:

Zinc, per cent.....	15-50
Tin	Remainder

Tin-Zinc-Aluminum solders:

Zinc, per cent.....	8-15
Aluminum, per cent.....	5-12
Tin	Remainder

4. "The higher the temperature at which the 'tinning' is done, the better the adhesion of the tinned layer. By using the higher values of the recommended zinc and aluminum percentages given above, the solder will be too stiff at lower temperatures to solder readily and the workman will be obliged to use a higher temperature, thus securing a better joint. A perfect union between solder and aluminum is very difficult to obtain.

5. "The joint between previously tinned surfaces may be made

by ordinary methods and with ordinary soft solder. Only the 'tinning' mixture need be special for aluminum."

6. "There is no reason why a good solder for aluminum need be brittle as several commercial varieties are, and it is very undesirable that it should be."

7. "The tensile strength of a good aluminum solder is about 7,000 lbs./sq. in., those with higher tensile strength have, in general, their

TABLE 22.—ALUMINUM SOLDERS

Purposes (Names)	Per cent Zn	Per cent Sn	Per cent Al	Per cent Cd	Per cent Cu	Per cent
Bourbouze's A.S.		83.0	17.0			
Bureau of Standards, No. 1 *	8.0	78.0	9.0	5.0		
Bureau of Standards, No. 3 *	9.0	86.0	5.0			0.25 Ph
Bureau of Standards, No. 4 *	9.0	86.0	5.0			
Sterling's A.S.*	15.2	61.6	11.2		2.5	{ 1.2 Sb 8.3 Pb
Crown's A.S.*	18.0	63.0	13.0		3.0	{ 1.0 Pb 2.0 Sb
Richard's A.S.	19.04	78.34	2.38			0.24 Pb
Gopman's A.S.	20.31	49.05				26.06 Ph
Seifert's A.S.*	21.0	73.0				5.0 Pb
Burgess' *	21.0	76.0	3.0			
Richard's A.S.*	31.0	63.0	3.0			3.0 Ph-Sn
So-Luminum *	33.0	55.0	11.0		1.0	
Auel's A.S.*	35.0	63.0	0.25		2.0	
Wuest's *	50.0		30.0		20.0	
Mourey's A.S.	50.0		30.0		20.0	
Roesch's A.S.*	50.2	48.6			0.2	0.7 Sb
Wuest's *	65.0		20.0		15.0	
Bureau of Standards Zn 1*	75.0		5.0	20.0		
Mouray's A.S.	80.0		12.0		8.0	
Mouray's A.S.	85.0		9.0		6.0	
Mouray's A.S.	87.0		9.0		4.0	
Mouray's A.S.	88.0		7.0		5.0	
Mouray's A.S.	89.5		7.0		3.5	
Mouray's A.S.	90.0		6.0		4.0	
Mouray's A.S.	91.3		6.0		2.7	

* Government Publication No. 41, p. 33.

temperature of complete liquation too high for soldering purposes. The strength of a joint depends upon the type and upon the workmanship. Much dependence should not be placed on the strength of a joint."

Fluxes are not used, as a rule. The solder is applied to the preheated surfaces of the base metal with the torch, the heat of the soldered article sufficing to melt the solder alloy, which is rubbed in with a wire brush. A soldering iron is only used for joining very small articles.

Table 22 on preceding page gives a list of the aluminum solders described in literature.

CHAPTER V

PEWTER

The original pewter, as used for the manufacture of plate and drinking vessels for many hundred years, consisted of 80 per cent of tin and 20 per cent of lead, containing various quantities of antimony and copper as well as traces of other constituents such as iron, zinc, etc. Cheaper grades of this alloy, or group of alloys, contained as high as 50 per cent lead, while the highest types of pewter consisted principally of tin, containing but small percentages of lead and copper, added to make the metal harder and more sonorous. In later years, when the poisonous properties of lead became to be realized, the percentage of lead contained in alloys used for the manufacture of drinking vessels and similar articles was fixed by the legislatures of the different countries, the standard percentages originally decided upon ranging from 12 to 16 per cent. These percentages were gradually lowered in practically all countries, until today the maximum lead contents of pewter for containers of food and beverages are almost universally fixed at 10 per cent. An alloy of this composition is practically insensible to the corrosive action of any acid foods and beverages, including vinegar.

Antimony, copper, and bismuth were almost invariably added in gradually increasing percentages to harden the alloys, the quantity of bismuth having been limited by its comparatively high price—if compared to lead and antimony—while excessive amounts of copper causes the metal to turn reddish or brown.

The percentages of antimony present in pewter finally increased to a point where this element became the chief alloying constituent besides tin, a few per cent of lead being retained to improve the fluidity of the metal, until with the introduction of Britannia metal, the practical importance of pewter as a distinctive group of tin alloys vanished entirely. The alloys now produced and known by the name of "pewter" are essentially tin-antimony-copper alloys, closely resembling high grade Britannia metals.

Table 23 indicates the composition of a few pewter alloys produced in England and on the Continent.

TABLE 23.—PEWTERS

Per cent Sn	Per cent Sb	Per cent Cu	Per cent Pb	Per cent Zn	Per cent Bi
80.0			20.0		
73.5	5.5	1.0	20.0		
88.42	7.16	3.45		0.88	
89.3	7.6	1.8	1.8		
87.2	5.7	1.6	11.5		
84.7	1.7	6.8			6.0
90.1	6.3	3.1		0.5	
90.0	6.0	2.0			2.0
90.0	7.0	3.0			
89.4	7.0	1.80	1.80		
81.2	5.7	1.60	11.15		
86.3	6.6	1.60		3.06	1.60

TABLE 24.—TUTANIA ALLOYS

Purposes (Names)	Per cent Sn	Per cent Sb	Per cent Cu	Per cent Pb	Per cent Zn	Per cent Bi
German Tutania.....	91.4		0.7	7.6	0.3	
Cast Tutania.....	91.4		0.7	7.62	0.25	
Cast Tutania.....	88.5		3.5	7.1		0.9
English Tutania.....	80.0	16.0	2.7		1.3	
English Tutania.....	25.0	25.0		25.0		25.0
				Brass		
Cast Tutania.....	92.4	4.6	2.5	0.32		
Plate Tutania.....	90.0		2.7	6.0	1.3	

CHAPTER VI

BRITANNIA METAL

The most important of the tin antimony alloys is Britannia metal, a group of alloys which derive their name from the original French term "*métal anglais*." Indeed, it appears that while originated in England, these alloys were also produced in France, and the first, although meager, description of this series of alloys is found in a French book on alloys published by Guettier in 1870. One or two German publications also mention Britannia metals before any definite reference to these alloys was made in English or American technical publications.

Nevertheless, Britannia Metals are doubtlessly of British origin, having been introduced about the middle of the 18th century as possessing better mechanical properties than pewter, which previous to the introduction of Britannia alloys was universally used for the casting and shaping of table ware, plate, beer pots, and similar articles.

While, theoretically, Britannia metal may be considered tin hardened by the addition of small quantities of antimony, these alloys usually contain from 1 to 3 per cent of copper and small amounts of lead and iron. Occasionally, they also contain from 0.5 to 2.0 per cent zinc and bismuth. Certain alloys such as the various Mino-for compositions, Birmingham II, etc., contain considerable amounts of zinc, others run high in bismuth or lead, but all these alloys do not represent genuine Britannia metals and should therefore be termed "Britannia-like Alloys."

Britannia metal has a silvery color with a bluish tinge, unless a considerable percentage of copper is present, which tends to impart a yellowish tint to the color. The metal takes a high polish, and is hard, malleable, and ductile. The hardness of the alloys is directly proportional to the quantities of antimony and copper present, but may be greatly influenced by the pouring methods and the subsequent heat treatment applied.

The pouring temperature of Britannia alloys is about 75 to 100° C. above melting temperatures (240 to 250° C.), ranging between 315 to 330° C. (600 to 625° Fahr.). A practical indication of this temperature is the light blue coloration of the freshly skimmed surface of the bath of metal. Yellow and purple colors are formed at lower temperatures.

The rate of cooling of the castings is of definite—although slight—influence on the hardness of the alloys, rapidly cooled castings being harder than slowly cooled articles. Of much greater importance is the effect of heating and cooling treatments. If, for instance, the alloy is heated to 200° C. for a short time, and is then cooled down gradually, the article has lost much of its original hardness, while on rapid cooling, as, for instance, by quenching, the hardness of Britannia metals is considerably increased.

Although straight Britannia alloys are much better adapted to mechanical working than tin lead alloys such as the original pewter alloys and Biddery metals, they are always more or less brittle, so that, wherever possible, articles are produced by direct casting.

Articles of complicated shape may be cast in a number of separate molds, the several parts being assembled and put together by soldering with high grade solders of exactly identical color, or in one mold constructed of a number of parts. To prevent the alloys from adhering to the walls of the mold, these must be coated with a smooth and uniform layer of lamp-black, best results being obtained by holding the cold mold over the dull flame of an ordinary lamp filled with turpentine. The mold is then heated to within 50° C. (120° Fahr.) of the pouring temperature of the alloy, and the metal poured. Molds made of brass are generally used for this purpose, which, apart from giving clean and smooth castings, exhibit the correct degree of thermic conductivity required to obtain best mechanical properties.

It is obvious that on account of the crystalline nature of the surface of cast Britannia articles, these are bound to present an unsightly and unfinished appearance, thus necessitating a suitable finish-treatment by polishing either on a lathe provided with wooden discs covered with leather, or, if the shape of the castings does not lend itself to this treatment, by means of a burnisher.

For stamping and other mechanical treatments of Britannia alloys, the metal is either cast in open cast iron molds of the required width, or the bars are first cross-rolled to obtain the width desired, straight rolling this product to the required gauge. The ingots may

be rolled cold or hot and reduced to 1/10 of their original thickness in about 10 passes without inducing appreciable hardening. Indeed, it appears that the general effect of the rolling treatment of Britannia metals is to soften rather than to harden the alloys, and no annealing is therefore required during the rolling process.

TABLE 25.—BRITANNIA METAL

Purposes (Names)	Per cent Sn	Per cent Sb	Per cent Cu	Per cent of other elements
Britannia:				
English.....	94.0	5.0	1.0	
German.....	93.65	3.70	2.65	
Sheet.....	91.5	7.1	1.4	
Plate.....	90.62	7.81	1.46	
Cast.....	90.6	9.2	0.2	
Cast.....	90.71	9.20	0.09	
Sheet.....	90.6	7.8	1.6	
Cast-English.....	90.1	6.3	3.1	0.5 Zn
English.....	90.0	7.0	3.0	
English.....	90.0	6.0	2.0	2.0 Bi
English.....	89.3	7.0	1.8	1.8 Pb
Spoons.....	88.5	11.4	0.15	
Spoons.....	88.4	8.7	2.9	
Brittle.....	85.6	9.6	0.8	3.0 Zn, 0.8 As
English.....	85.5	9.6	1.8	3.1 Zn
Cast.....	85.5	10.5	1.0	3.0 Zn
Cast.....	85.4	9.66	0.81	3.06 Zn
Spoons.....	85.4	14.4	0.16	
Table Utensils.....	84.86	5.02	3.68	4.88 Bi
Spoons.....	84.7	5.0	3.7	1.0 Zn, 4.9 Bi
German.....	84.0	9.0	2.0	5.0 Zn
Castings.....	81.9	16.2	1.8	
English.....	81.2	5.7	1.6	11.5 Pb
English.....	80.0	10.0	9.0	1.0 Pb
English.....	75.0	8.5		8.0 Pb, 8.5 Bi
Cheap.....	72.0	24.0		4.0 Bi

Influence of Other Metals.—Of the various metals added to straight Britannia alloys, that is to say, to the original Britannia compositions consisting of tin and antimony, copper in amounts of from 0.5 to 3 per cent is practically always present. Although in

addition to increasing the hardness this element tends to lower the ductility of Britannia metals, the latter influence becomes pronounced only if more than 3 or 4 per cent copper is present.

Zinc, which is frequently added for economy's sake, is more or less objectionable in any amount, although the increase of hardness and brittleness induced by larger percentages of this metal can be considerably modified by a reduction of the antimony contents. Alloys such as the Minoform metals, which besides 9 and 10 per cent zinc contain as high as 17 to 20 per cent antimony, are not true

TABLE 26.—BRITANNIA-LIKE ALLOYS

Names	Per cent Sn	Per cent Sb	Per cent Cu	Per cent of other elements
Queen's Metal.....	80.5	16.5	3.5	
Queen's Metal.....	87.0	8.5	3.5	1.0 Zn
Queen's Metal.....	88.5	7.0	3.5	1.0 Bi
Queen's Metal.....	88.5	7.1	3.5	0.9 Zn
Minoform.....	66.0	20.0	4.0	9.0 Zn
Minoform.....	67.53	17.0	3.26	8.9 Zn
Minoform.....	68.5	18.2	3.3	10.0 Zn
Minoform.....	66.0	20.0	4.0	9.0 Zn
Ashberry Metal.....	79.0	15.0	3.0	2.0 Zn
Ashberry Metal.....	80.0	14.0	2.0	1.0 Zn
Algiers Metal.....	90.0	10.0		
Algiers Metal.....	75.0	25.0		
Birmingham I.....	90.57	9.38	0.03	
Birmingham II.....	85.5	10.5	1.0	3.0 Zn
Birmingham.....	90.6	7.8	1.5	
Birmingham.....	90.71	9.2	0.1	
Métal Argentine.....	94.5	5.0	0.5	
Métal Argentine.....	97.3	2.0		0.7 Bi
Bechmann Bronze.....	96.9	2.9	0.2	
Kaiserzinn.....	93.0	5.4	1.6	
Poterie d'Étain.....	90.0	9.0	1.0	
Hanover White Metal....	86.8	7.6	5.6	
Koeller's Alloy.....	85.7	10.4	1.0	1.8 Bi
Wagner's Alloy.....	85.64	9.66	0.81	3.06 Zn, 0.83 Bi
Karmarsch's Alloy.....	85.0	5.0	3.6	1.4 Zn, 1.6 Bi
Jacobi's Alloy.....	85.0	10.0	5.0	
Prince's Metal.....	84.8	15.2		
Ludenscheidt Plate.....	71.85	24.26	3.85	Tr. Pb
Dutch White Metal.....	81.5	8.8	9.6	

Britannia metals, and the effect of the different constituents of these alloys on their mechanical properties are governed by different principles. The effects of iron are similar to those of zinc, although comparatively small percentages of this element will induce an excessive degree of hardness and brittleness. The same is true of arsenic, of course, and these two elements should never be found in Britannia metals.

Lead may be used to advantage for castings, improving as it does the fluidity of the metal. Larger quantities of lead should not be added to Britannia alloys, however, since apart from spoiling the color and luster of the surface, it tends to lower the resistance of Britannia metal to atmospheric corrosion.

Tables 25 and 26 give the composition of the most important Britannia and Britannia-like alloys mentioned in literature.

CHAPTER VII

FUSIBLE ALLOYS

The term "fusible alloys" is generally applied to all the binary, ternary, and quaternary alloys of tin, bismuth, cadmium, and lead melting at lower temperatures than tin. A considerable number of these alloys melt at temperatures lower than the boiling point of water, but the majority of the commercial types of fusible metals, which, besides having low melting points, must possess certain mechanical properties such as tenacity, strength and a definite degree of hardness, melt at temperatures of from 100 to 175° C. (212 to 350° Fahr.).

Practically all the fusible alloys represent the eutectic compositions of their specific group of mixtures, unless this composition is modified in order to attain certain mechanical or physical properties.

The composition and melting points of the eutectics of the important binary alloys are given in table 27.

TABLE 27

Bi : Sn :: 43.0 : 57.0	137° C.
Bi : Pb :: 56.5 : 43.5	125° C.
Bi : Cd :: 55.5 : 44.5	146° C.
Sn : Pb :: 75.0 : 25.0	180° C.
Sn : Cd :: 67.6 : 32.4	177° C.
Pb : Cd :: 63.0 : 37.0	249° C.

The most important binary alloys are those of tin and bismuth and of lead and bismuth, all of which may be alloyed by simple fusion and without taking any special precautions. For most practical purposes, however, the ternary alloy of these elements, lead-tin-bismuth, is used, since apart from the lower melting points of these alloys, these may be much better adapted to various uses and conditions, while tin-lead-bismuth alloys are obviously cheaper than the respective tin-bismuth alloys possessing similar melting points and mechanical properties. The most fusible of this ternary group

of alloys is generally assumed to consist of equal parts of lead and tin, and twice this quantity of bismuth (25% Pb, 25% Sn, 50% Bi), which melts at 94° C. (201° Fahr.). This alloy, known as Darcey's Alloy, possesses the peculiar property of dilating in an anomalous manner when heated, expanding regularly from 32° to 95° C., and contracting gradually with increasing temperatures to 131° C. At this temperature, the volume of this alloy is less than at 32° C., while above 131° C. expansion continues regularly, becoming uniform at temperatures above 174° C. This property of expanding when cooled from 131 to 95° C. makes Darcey's alloy eminently useful for taking impressions from dies, the thinnest lines being reproduced with extreme clearness and accuracy. This property, which is attributed to the effect of latent heat, disappears after reheating the solid alloy three or four times, but may be restored by re-melting.

Other alloys, exhibiting the same property of expanding on cooling while in a soft state are given in table 28. These alloys are used for the production of delicate castings.

TABLE 28

Per cent Bi	Per cent Sn	Per cent Pb
27.27	13.64	59.08
50.00	20.00	30.00
50.00	25.00	25.00
50.00	18.75	31.25

Parkes and Martin have published a table of alloys with definite melting points that are useful for tempering steels. The results, calculated in percentages, are given in table 29.¹

The articles to be tempered are placed on the solid alloy which is then heated to complete fusion. At this time the articles are of the required temper, and are quickly cooled in water. The cheaper lead bismuth alloys are inferior for this purpose, being too rapidly oxidized and tending strongly to separate out on cooling. According to Hiorns, a number of bismuth tin alloys are better suited for tempering tools. Table 30 gives the compositions and melting points of three alloys of this group.

¹ Sexton, Alloys, p. 208.

TABLE 29

Per cent Bi	Per cent Pb	Per cent Sn	Melting points	
			Degrees C.	Degrees F.
50.0	31.2	18.8	94	202
47.0	35.5	17.7	98	208
42.1	42.1	15.8	108	226
40.0	40.0	20.0	113	236
36.5	36.5	27.0	117	243
33.3	33.3	33.3	123	254
30.8	38.4	30.8	130	266
28.5	43.0	28.5	132	270
25.0	50.0	25.0	149	300
23.5	47.0	29.5	151	304
22.2	44.4	33.4	143	290
21.0	42.0	57.0	143	290
20.0	40.0	40.0	145	292
19.0	38.0	43.0	148	298
18.1	36.2	45.7	151	304
17.3	34.6	48.1	155	312
16.6	33.2	50.2	158	316
16.0	36.0	48.0	155	312
15.3	38.8	45.9	154	310
14.8	40.2	45.0	153	308
14.0	43.0	43.0	154	310
13.7	44.8	41.5	160	320
13.3	46.6	40.1	165	330
12.8	49.0	38.2	172	342
12.5	50.0	37.5	178	352
11.7	46.8	41.5	167	332
11.4	45.6	43.0	165	328
11.2	44.4	44.4	160	320
10.8	43.2	46.0	159	318
10.5	42.0	47.5	160	320
10.2	41.0	49.8	161	332
10.0	40.0	50.0	162	324

TABLE 30

Per cent Bi	Per cent Sn	Melting points	
		Degrees C.	Degrees F.
50	50	160	320
33	67	166	332
20	80	200	392

TABLE 31.—FUSIBLE ALLOYS

Names	Per cent Cd	Per cent Bi	Per cent Sn	Per cent Pb	Degrees F.
Wood's Alloy.....	10.0	50.0	13.3	26.6	140
	10.0	45.0	15.0	30.0	149
	12.0	60.0	16.0	12.0	150
	7.0	52.2	14.8	26.0	155
	7.1	50.0	14.3	28.6	158
	10.10	49.5	13.13	27.27	158
	12.5	50.0	12.5	25.0	158
Eutectic.....	10.0	50.0	13.3	26.7	158
	10.1	49.5	13.1	27.3	158
	15.4	38.4	15.4	30.8	160
	12.4	50.0	12.5	25.0	160
	34.5	27.6	10.3	27.6	167
	8.6	57.1	11.45	22.85	167
	8.85	44.15	23.5	23.5	167
	6.25	50.0	9.37	34.38	170
		42.1	15.8	42.1	174
	9.5	35.35	20.05	35.1	176
	11.55	57.65	15.4	15.4	176
	15.4	38.4	15.4	30.8	176
Wood's Alloy.....	7.14	50.0		42.86	180
Hauer's Alloy.....	16.67	33.33		50.0	193
Lichtenberg's.....	50.0	20.0	30.0		197
Eutectic Alloy.....	8.1	51.6		40.2	197
Darcet's Alloy.....		50.0	25.0	25.0	200
Non-Corrosive.....		52.5	15.5	32.0	200
Rose's Alloy.....		42.85	15.92	27.93	201
		42.1	42.1	15.8	201
		50.0	25.0	25.0	201
Newton's Alloy.....		50.0	18.75	31.25	203
	14.3	33.6	19.0	33.1	203
	11.11	55.56	33.33		203
	16.67	50.0	33.33		203
	25.0	50.0	25.0		203
		52.5	15.5	32.0	204
Rose's Alloys.....		50.0	22.0	28.0	212
		50.0	18.75	31.25	212
Eutectic Alloy.....	20.0	54.0	26.0		217
		40.0	20.0	40.0	236
Bismuth Solder.....		39.02	22.14	38.84	255
		30.8	38.4	30.8	266
		63.74	36.26		280
Bismuth Solder.....		33.33	33.33	33.33	284
Bismuth Solder.....		24.24	27.51	48.25	293
Eutectic Alloy.....	18.0	50.0	32.0		293
Bismuth Solder.....		31.93	36.25	31.80	302
Bismuth Solder.....		17.58	29.92	52.80	311
		46.85	53.15		315
Bismuth Solder.....		13.79	31.30	54.90	320
		18.06	81.94		390

Some well known tin-lead-bismuth alloys are "Newton's metal," "Rose's alloys," and "Lichtenberg's metal," which on account of their low melting points and favorable mechanical properties are extensively used as soft solders for pewter and similarly alloyed articles. The composition and melting points of these alloys are given, together with a large number of other fusible alloys, in table 31. The use of these alloys in the preparation of the so-called safety plates, which were inserted in the tops of steam boilers, has, according to Vickers,¹ been almost entirely abandoned, since boilers provided with these plates have been found to explode without a previous melting of the plates. Chemical and physical examinations have shown that long-continued heating of the plates causes the formation of alloys within these safety plates whose melting points are much higher than those of the compositions originally used. Vickers mentions a number of alloys which are said to melt, if the pressure of the steam exceeds a certain maximum. Table 32 gives the composition of these alloys, calculated in percentages, and the corresponding steam pressures.

TABLE 32

Per cent Bi	Per cent Pb	Per cent Sn	Melting point, Degrees F.	Steam pressure, in pounds
50.0	31.2	18.8	202	15.0
40.0	40.0	20.0	236	22.5
33.3	33.3	33.3	254	30.0
30.8	38.4	30.8	266	37.5
28.5	43.0	28.5	270	45.0
21.0	42.0	57.0	290	52.5
22.2	44.4	33.4	290	60.0
14.8	40.2	45.0	308	75.0
10.5	42.0	47.5	320	90.0
10.2	41.0	49.8	332	105.0
12.8	49.0	38.2	342	120.0

Certain compositions of the lead-tin-bismuth group of alloys are also used extensively as Cliché metals. Table 33 gives the composition of a number of these alloys employed in this country and in Europe.

If used for rollers for printing cotton goods, Cliché metals usually contain from 10 to 16 per cent antimony, which in hardening the

¹ Vickers, *Metals and Their Alloys*, p. 583.

TABLE 33

Per cent Sn	Per cent Pb	Per cent Bi
25.0	25.0	50.0
18.75	31.25	50.0
18.18	27.27	54.55
22.22	22.22	55.56
21.43	50.0	28.57

alloy produces a considerable increase of resistance to wear. Table 34 gives the composition of a number of antimonial Cliché metals.

TABLE 34

Per cent Sn	Per cent Pb	Per cent Sb	Per cent Bi
48.0	32.5	10.5	9.0
48.5	30.3	12.1	9.1
18.75	31.25	12.5	37.5
21.05	21.05	15.80	42.10

Bismuth-Lead-Tin-Cadmium Alloys.—The melting points of the ternary bismuth-lead-tin alloys are still further lowered by the addition of cadmium, and a number of well known fusible alloys consist of various proportions of these four metals. The eutectic of the quaternary alloys consists of

10.10% Cd, 13.13% Sn, 27.27% Pb, 49.5% B

and melts at 70° C. (158° Fahr.). According to N. F. Budgen,¹ it is unlikely that ternary or quaternary compounds are really formed and the development of heat observed in many of the alloys at 95–100° C. or 110–115° C. is to be attributed entirely to changes in the binary solid solutions, as it always diminishes towards the interior of the tetrahedron representing graphically the quaternary systems. Table 35 gives a number of alloys of lowest melting and freezing points published by Budgen, and it is seen that several of these have a somewhat lower point of initial melting than the eutectic

¹ J. Soc. Chem. Ind. (England) 1924, 27 pp. 200T–203T.

alloy. According to Budgen, this difference may be due either to inaccuracies of temperature measurements or to the influence of surfusion phenomena.

Some of the cadmium alloys are readily soluble in boiling water, while apart from lowering the melting points, cadmium possesses the advantage of decreasing the brittleness introduced by bismuth contents. The chief uses of cadmium-tin-bismuth-lead alloys are for fusible metal seats in automatic fire extinguishers, for castings requiring low temperatures, and for dental purposes, that is, for filling hollow teeth.

TABLE 35

Composition, per cent				Breaks in the cooling curves, degrees C.			
Cd	Pb	Sn	Bi	1	2	3	4
1.5	34.0	4.5	60.0	98	92	80	
12.9	21.4	5.7	60.0	101	85	71	
11.8	19.6	8.6	60.0	100			70
10.7	17.9	11.4	60.0	100		78	70
12.5	30.0	7.5	50.0	100	90	70	
9.4	31.9	5.6	53.1	100	80	75	
13.1	24.4	21.9	40.6	100	87		69
11.25	26.25	18.75	43.75	85	68		65
9.4	28.1	15.6	46.9	75		68	66
7.5	30.0	12.5	50.0	73		68	66
5.6	31.9	9.4	53.1	77		70	68
3.75	33.75	6.25	56.25	90		72	68

A very interesting application of fusible metals of very low melting points is related by Budgen.¹ During the war years petrol tanks of complicated form were required free from joints and seams for aeronautical work. These were made by electrodepositing copper upon a casting of fusible metal, and then by placing the whole finished article in hot water the fusible alloy was run out, leaving a copper shell intact.

Mercury Alloys.—Lowest melting and freezing points of fusible alloys are attained if mercury is added to the binary, ternary, and quaternary alloys of the metals composing fusible alloys, although

¹ Loc. cit.

other metals are also added occasionally to obtain certain mechanical properties. Alloys of this type are not, as a rule, distinguished by low melting points, however, but are generally characterized by their high degree of plasticity, followed by gradual hardening. The binary alloys of the metals with mercury are generally termed "Amalgams."

One of the most important fusible binary mercury alloys is cadmium amalgam which is chiefly used for teeth filling and for the preparation of metallic cements. Cadmium readily combines with mercury and the alloys may be prepared either by rubbing the finely divided cadmium with mercury in the cold and removing the excess mercury by pressing the mass in chamois bags, or by introducing powdered cadmium or very thin cadmium sheet into a bath of mercury heated to just below the boiling point.

Cadmium and zinc form two series of mixed crystals. The first series, containing from 0.0 to 75 per cent cadmium, melts at temperatures of from 38.8 to 188° C. (incipient fusion), while the second series of mixed crystals, containing from 77 to 100 per cent atomic per cent of cadmium, begins to solidify between 188 and 320.8° C. Cadmium-mercury alloys consisting of equal parts of the two metals, or of from 74 to 78 per cent mercury and from 22 to 26 per cent cadmium are of wax-like consistency if moderately heated. After some time, the mixture becomes crystalline and assumes a comparatively high degree of hardness. Addition of tin or bismuth to these alloys increases their plasticity. The following two binary mercury alloys are recommended for filling teeth:

1. 25.99% Cd, 74.01% Hg
2. 21.74% Cd, 78.26% Hg

Tin amalgams are usually prepared by rubbing powdered tin with mercury and removing the excess of mercury by pressing in chamois bags. The constitution of tin-mercury alloys has been studied by Puschin and Van Heteren.¹ In alloys containing up to 15 per cent mercury, crystals composed either of pure tin or of mixed crystals containing small amounts of mercury, separate out on cooling, while at higher percentages of mercury, up to 75 per cent, a compound— Hg_3Sn —is formed, the alloys within this range consisting of a mixture of this compound and tin crystals. Above 75 per cent mercury the alloys consist of the compound and mercury.

While formerly, tin-mercury alloys were extensively employed for

¹ Ztschft. f. Anorg. Chem., 1903, p. 207.

the coating of mercury, which is now being accomplished much simpler and cheaper with thin layers of silver, tin amalgams are now employed for filling teeth, although instead of the binary alloys, ternary mercury alloys containing tin and cadmium appear to be generally preferred. Varrentrap's dental alloy consists of one part of cadmium and two parts of tin dissolved in an excess of mercury.

Bismuth amalgam, obtained by adding mercury to molten bismuth is distinguished by an exceptionally high degree of fluidity, and is therefore used for filling out very delicate designs, or organic tissue in the manufacture of anatomical preparations.

An alloy composed of equal portions of bismuth, tin, and lead, dissolved in nine times their weight of mercury is used for silvering curved mirrors. The glass is carefully heated to fit the temperature of the amalgam, prepared by adding the mercury to the molten lead-tin-bismuth alloy, a small quantity of the mixture poured into the cavity of the article and swung to and fro until the entire surface is covered.

The fusible ternary and quaternary alloys are frequently provided with additions of mercury ranging from 5 to 15 or even 20 per cent of mercury to decrease the melting point and to increase the fluidity of the alloys. Table 36 gives some of the comparative figures obtained

TABLE 36

Composition of alloys, per cent				Temperature of complete solidification, degrees C.	
Pb	Sn	Bi	Cd	Without Hg	With Hg
25.0	12.5	50.0	12.5	68.5	56.0
26.7	13.3	50.0	10.0	68.0	56.0
26.0	14.8	52.2	7.0	68.0	Not determined
28.6	14.3	50.0	7.1	67.5	53.0
27.6	10.3	27.6	34.5	71.0	62.0
35.1	20.05	35.35	9.5	67.0	56.0
27.27	13.13	49.5	10.10	65.5	55.0
33.1	19.0	33.6	14.3	70.0	60.0
22.85	11.45	57.1	8.6	67.0	50.0
23.5	23.5	44.15	8.85	66.0	55.0
15.4	15.4	57.65	11.55	68.5	58.0
30.8	15.4	38.4	15.4	68.0	61.0

by Budgen¹ in determining the melting and freezing points of a number of ternary alloys before and after adding 16.6 per cent by weight of mercury.

By adding more mercury, the melting points of the alloys can be lowered to any desired degree until the alloy remains pasty or even liquid at room temperatures, approximately 50 per cent of mercury being required to attain this end.

The influence of mercury on the mechanical properties of the fusible metals is to decrease the tenacity, hardness and flexibility of these alloys, while the tendency to corrosion does not appear to be increased by mercury additions.

The chief uses of the mercury alloys of the fusible metals are for the production of direct impressions of delicate plant and animal tissues and for the manufacture of small hollow statuettes.

¹ J. Soc. Chem. Ind. (England) 1924, 27, p. 200T.

CHAPTER VIII

SHOT

Shot metal mixtures consist of lead and small quantities of arsenic, while occasionally some manufacturers add small amounts of other metals such as copper and antimony. The percentage of arsenic required depends upon the size of the shot. Very small shot seldom contains more than 0.2 per cent arsenic. Coarse shot contains from 0.4 to 0.5 per cent arsenic, while the percentages of intermediate sizes run from 0.2 to 0.4 per cent arsenic. English manufacturers use about 10 parts of arsenic in 1100 parts of lead, while in France 8 parts of arsenic per 1000 parts of lead are usually considered sufficient.

Due to the toxicological properties of arsenic, the alloying of the mixtures must be carried out in well aired rooms and with furnaces supplied with sufficient draught. The lead is melted with oxide of arsenic and charcoal. Instead of oxide of arsenic, other arsenic compounds such as realgar are sometimes used for this purpose.

The lead is melted together first, covered with a thin layer of charcoal dust, and—on top of this—the requisite quantity of oxide of arsenic, which is again covered with a layer of crushed charcoal. The mass is then stirred with a wooden pole, and the pot closed with a well fitting cover, which for the sake of further security against the poisonous vapors emitted by the arsenic compounds is often luted around the edges with tough clay. The metal is heated three hours and cast. Since it is not economical to treat all the shot metal by this method, a very concentrated arsenic alloy is usually produced which serves as base alloy, from which the shot lead proper is then made up.

The small percentages of arsenic contained in the lead increase the fluidity and hardness of the latter, and tend to impart a more spherical shape. If the amount of arsenic is too small, the shot will not become entirely spherical.

The oldest method of producing shot, which is still being used to a large extent, is to let the metal drop from the top of a shot tower,

125 feet high, into water. The tower is subdivided into several floors, the largest sized shot being dropped from the top floor, while smaller shot is dropped from lower floors. The molten alloy is poured into a perforated iron basin, the perforations being regulated according to the size of the shot produced. The distance between the individual perforations should be about three times their diameter to prevent the descending drops of metal from touching each other, forming one mass. To prevent too rapid a flow of metal through the perforations, the bottoms of the pans are covered with a sludge of lead oxide. Apart from causing coalescence of the drops, an excessive rate of flow through the perforations would cause the formation of slightly oblong spheres.

While on account of the arsenic content the metal is quite fluid, some of the perforations, the diameter of which is noticeably smaller than that of the shot produced, tend to clog up, preventing the drops from dropping off properly and causing it to cling to the pan. The next drops add to the mass until, gradually, icicles are formed, which are scraped off at intervals, dropping into the water at the bottom of the tower.

Occasionally, the water is covered by a layer of oil, which is said to cause the shot to retain its spherical shape better than with plain water. Oxidation of the moist surface of the shot after being taken out of the water may be prevented by adding a fraction of a per cent of sodium sulphide to the water, which coats the shot with a film of dark gray lead sulphide unaffected by the atmosphere.

The water receiving the shot is frequently changed to prevent it from becoming too hot.

Dropped shot runs in size from diameters of 0.04 inch ("dust" to 0.23 inch ("FF"). Larger sizes are not produced by the dropping process but must be cast. About 4560 units of dust shot make one ounce. Of the FF-shot, 24 units weigh one ounce. BB-shot, measuring 0.18 inch in diameter, is somewhat lighter, 50 units of this size making one ounce. Buck-shot ranges from 0.24 to 0.44 inch diameter, three units of the largest size weighing one ounce.

The height of the shot tower may be considerably decreased if, according to D. Smith's (New York) method, the molten drops are made to fall through an ascending current of air. The height of the tower depends on the velocity of the ascending air currents, that is to say, the distance of the drop is determined by the number of the particles of air with which the shot comes into contact.

By a new process, the towers are eliminated entirely, the shot being produced by centrifugal force. A thin stream of metal is poured on a rapidly revolving disc, the shot being thrown against a screen. The size of the shot is determined by the speed of revolution of the disc, increasing with decreasing speeds.

Sorting the Shot.—After drying the shot, it is mixed with a small quantity of graphite to polish it. The material is then screened to remove coarse scrap and dust. It is then sorted by means of sorting drums provided with perforations corresponding to the different sizes of shot.

The “flat-foots” and “square heads” were formerly removed by rolling the shot down an inclined plane of polished iron or glass three to five feet in length. The perfectly spherical bodies roll in straight lines and are carried by their momentum over a trench about 4 to 5 inches wide into a bin. The imperfect shot, on the other hand, does not travel as freely and does not, therefore, gather enough momentum to be carried over the trench, being collected in a special bin. This first test is usually followed by a second, more difficult one, the shot being required to travel over a long, inclined plane consisting of four sections, which are separated from each other by trenches.

CHAPTER IX

THE MELTING AND REFINING OF WHITE METAL SCRAP

The various operations of residue and scrap melting works leading to the production of secondary metals and alloys include the following steps:

1. Grading and smelting the innumerable white metal residues towards the production of impure or pure intermediate metals and alloys.

2. Grading the metallic scrap procured in the market and subjecting this material to a refining or purifying treatment in blast or reverberatory furnaces.

3. Eventually, further metallurgical treatments towards the concentration or separation of certain components of intermediate alloys.

4. Alloying the various refined and prepared materials to attain the compositions required by the market, applying final refining treatments and casting.

5. Individual metallurgical treatment of the separated or compounded by-products of the above processes, returning the intermediate metallic products into the process.

The treatment of the common tin and white metal residues is described in another chapter. The products of the various processes, carried out in reverberatory and/or blast furnaces are obtained in various states of purity and containing all conceivable proportions of tin, lead and antimony, with smaller amounts of copper, zinc, arsenic, and other elements generally considered as impurities. The exact percentages, or the presence and absence of these are governed by the nature of the various processes employed.

The importance of correct and intelligent grading of the metallic scraps procured in the open market is obvious, and it is necessary not only to separate the materials rich in tin from the poorer grades, or to group the scrap in accordance with the various proportions of antimony-tin, antimony-copper-tin, etc., but to guard against the presence of scrap containing larger percentages of impurities such as

zinc, arsenic, etc. It is practically impossible, perhaps, to discover the presense of 1 or 2 per cent of zinc in some of the tin-base bearings contained in large lots of bearing metal scrap, but it is necessary to exclude all zinc-base material of any nature. Zinc-base bearing metals may easily be recognized, of course; but closer attention must be paid to other white metal scrap, poor and rich in tin, since even some alloys very rich in tin, such as Britannia or "Britannia-like" alloys, pewter and similar groups of alloys may carry zinc to the amount of from 5 to 10 per cent.

Apart from zinc, arsenic may be considered the most serious impurity present in the common run of white metal scrap. Iron, nickel, and copper are more easily removed, while any of them may be made to perform some useful work while being removed. Thus, tin-base white metals containing nickel may be melted together with similar material holding copper, nickel and copper assisting considerably in drossing each other. Coppery material mixed with similar grades of zincy white metal will produce a better separation of either impurity, and the iron in one grade of white metal scrap will assist in the removal of arsenic present in other material, while arsenic and nickel possess the same degree of affinity for one another. Copper, iron, and arsenic, if present together tend to form a dross, while in absence of arsenic, copper and iron do not act upon each other in any way. The reactions of copper, nickel, iron, and arsenic on one another become noticeable only at higher temperatures, that is to say, at red heat, while in their relation to zinc and antimony, separation by mutual drossing may only be effected at temperatures near the freezing point of the alloys.

There are a number of standard methods used for the purification and treatment of secondary metals and alloys, each of which is, or may be made, productive of specific results. It is self-evident, of course, that the choice of any one of these methods is dependent not only on the composition of the raw material, but on the prevailing conditions of the scrap and secondary metal markets in general. Processes which may be quite profitable during one limited period may prove to be absolutely useless under changed market conditions.

The various melting and smelting operations necessary are almost exclusively carried out in reverberatory and melting pot furnaces. Electric crucible- and oil-fired tiltable furnaces are rarely used in white metal work.

Reverberatory furnaces are employed for the general treatment

of large quantities of metal, for the elimination of larger percentages of the impurities, and for the complete removal of obstinate impurities such as arsenic and zinc, etc., and where metallurgical separation—liquation and segregation—processes are to be carried out on a large scale. It is obvious that in view of the specific characteristics of the numerous processes applied, a number of furnaces of different sizes and proportions are required to attain best results. Liquation processes require shallow inclining hearths; refining treatments are best carried out in long furnaces of medium depth, while a number of processes such as segregation and settling, fractional crystallizations, etc., give really satisfactory results only if carried out in deep-hearthed furnaces. Wherever possible, different furnaces should also be used for the treatment of alloys rich and poor in tin.

Melting pots are generally used for the melting, alloying and final refining of white metals and alloys. A number of liquation or segregation processes are also carried out in melting pots, if reverberatory furnaces are not available for this purpose. Where only small amounts of impurities such as copper (not over 0.2 per cent) or zinc (not over 0.1 per cent) are to be removed, this may also be carried out in melting pots.

Very little attention is usually paid to the construction and shape of melting pots best suited for the purpose in question. Most of the melting pots used are made too shallow, so that for refining processes, or wherever higher working temperatures are required, the surface area of the metal exposed to the oxidizing influence of the air is too large in proportion to the amount of metal treated. Figure 8 illustrates a normal semi-spherical melting pot for melting, alloying and refining white metals. While not too deep for comfortable operation, the dimensions of this pot affords a satisfactory ratio of metal surface to metal contents. The depth of melting pots of this type exceeds by about 6 to 10 inches the length of the radius of the pot at its rim, the exact proportions depending upon the capacity of the pots. With an inside diameter of 30 in., the depth of a pot should therefore measure about 21 in. A diameter of the pot of, say, 60 in. should be equivalent to a depth of $30 + 10 = 40$ in.

The walls of white metal melting pots should not be made uniform all over, but must increase in thickness towards the bottom, this increase being as gradual as possible so as to preclude the setting up of dangerous internal strains. The thickness of the walls of a melting pot holding about 7000 pounds of lead or a correspondingly

smaller amount of white metal, should be about $1\frac{1}{2}$ in. at the rim and 2 in. at the bottom. The rim of this pot should be made about 6 in. wide and $1\frac{1}{2}$ in. thick. Very large pots, that is to say, such holding about 15,000 pounds and more should be supplied with a supporting flange about midway between rim and bottom. Figure

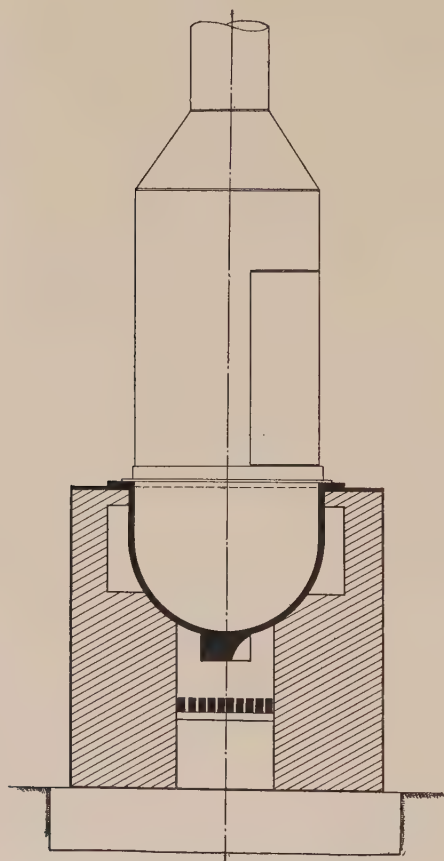


FIG. 8.—COMMON MELTING POT FURNACE.

9 shows the design and measurements of this type of melting pot and the general arrangement of the furnace. It is seen that instead of the one flue channel used in small melting pot furnaces, larger units of this type are usually supplied with two flues in order to better utilize the heat.

The opinion of some metallurgists that melting pot furnaces constructed as shown in Figures 8 and 9 do not heat up as fast as the simpler type of furnace consisting of the grates and four straight

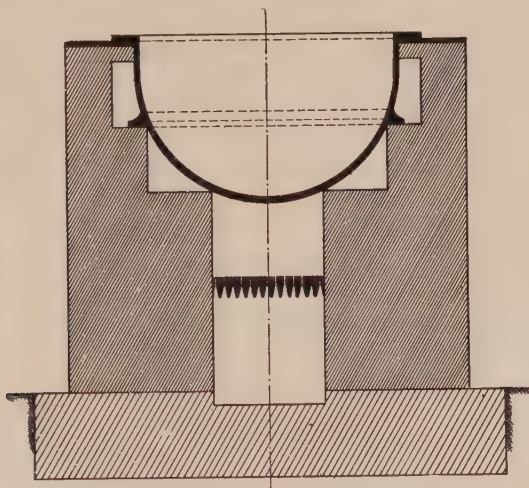


FIG. 9.—LARGE CAPACITY MELTING POT FURNACE.

walls is due to a lack of draught only. Where sufficient draught power is available, the construction of flues around the wall of the melting pots is bound to increase the heat efficiency of the plant. If the draught represents a factor of doubt, simple melting furnaces without flues should be constructed.

A more complicated variety of semi-spherical melting pots is the type shown in Figure 10. This may be used with advantage where small quantities of lead or white metals are to be melted and tapped quickly, as for instance, in tube and wire works, etc. This type of melting pot has also proved valuable in melting processes based upon the principle of segregation of metallic compounds of different specific weights, where the heavier constituents may be removed from the pot without disturbing the upper layers. The opening and closing of the outlet at the bottom of the pot is effected by means of a steel stopper moved by handwheel and screw.

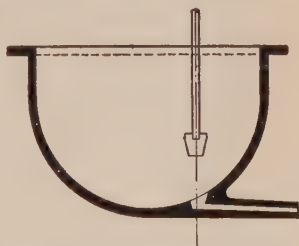


FIG. 10.—WHITE METAL MELTING POT WITH TAP ARRANGEMENT.

It will be recognized that this type of melting pot bears a close resemblance to the tapping pots used in copper and lead smelters for the separation of metals and metallic compounds from slag. However, since in the case of slag pots of this construction it is only necessary to separate a liquid substance from a solid, the outlets are usually closed with clay plugs which at the proper time are pierced by means of steel rods. Wherever it is necessary to separate liquids, however, a more elaborate closing device must be employed, and it appears that the steel stopper device moved by handwheel and screw is the most simple and, at the same time, effective contraption possible.

In general melting work where the temperatures are relatively high this type of melting pot should not be used, the characteristic shape of the walls rendering it too weak physically to withstand successfully the internal strains caused by such temperatures. The same is true where the white metal is to be subjected to a thorough refining process.

Another type of melting unit often found in white metal melting plants is the liquation furnace, which consists in principle of a liquating pan, a small firing arrangement, and a small melting pot in front of the furnace. Instead of the shallow, concave bottomed, iron box formerly used as liquating pan, which, on account of the heating strains invariably set up along the bottom section, tended to crack at the slightest provocation, this type of furnace has proved very successful. The hearth is made up of two iron plates resting obliquely upon a central collecting trough slightly inclined towards the melting pot placed in front of the furnace and directly below the lower end of the trough. The liquated metal is thus made to flow over the plates, heated from below, into the trough and, finally, into the melting pot.

In view of the moderate heat required, only a narrow fire space, located at the low end of the trough, is necessary, although this should be carried over the entire width of the furnace in order to obtain uniform heating of the plates. The hot gases of combustion are drawn into the flue at the other end of the furnace, the uppermost layer of the brickwork being constructed so as to leave about 5 in. of the plates unheated by direct action of the flue gases. Thus it is possible to obtain a uniform and easily regulated heating surface ranging from 350 to 900° Fahr. The ideal fuel for this type of liquating furnace is a soft long-flamed coal, best results being obtained with brown coal or peat.

A more solid type of liquating furnace is shown in Figures 11 and 12, the operation of which is obvious. It is important to have the hearth of the liquating furnace decline towards the fire-bridge since apart from the fact that the raw materials is removed from the direct neighborhood of the fire, permitting of a much better regulation and control of the heat, the liquated material flows towards the hottest part of the hearth, thus avoiding the constant danger of freezing always present if the liquated metal flows away from the fire bridge and towards the cool end of the furnace.

Figures 13 and 14 represent an interesting combination of zinc distillation and liquation furnace used in a number of Continental smelters. In view of the high temperatures of the zinc distillation process the liquation temperatures are too high for ordinary low-temperature liquation, of course and this furnace may only be used for the liquation of rather hard metals. In a number of instances, it is employed for the liquation of the argentiferous litharge produced in the cupellation of the argentiferous lead obtained by the distillation of rich zinc crusts (page 209).

Preliminary Refining Treatment of White Metal Alloys.—Practically all white metal alloys scrap purchased in the open market, with the exception, perhaps, of the various tin solders, is contaminated with one or more elements such as copper, zinc, iron, arsenic, etc., which, having served some specific purpose in the materials in question, are now looked upon as impurities. It is unsafe under all ordinary circumstances to retain these elements for use in secondary metals since, apart from the excessive drossing usually experienced with secondary metals of this type, the presence of copper, zinc, arsenic, etc., in white metals renders effective cleaning of the semi-finished product by steaming or fluxing impossible.

Ordinarily, the elimination of the impurities is carried out in the following order:

Copper (Iron, Nickel) by liquation and sulphurizing,
Zinc, by oxidation or steaming,
Arsenic, by washing with iron scrap.

If *sulphur* is present in the raw material, this is removed with the copper. If copper is present in small amounts only, it is eliminated together with the zinc, while the washing treatment with iron is also inductive to the removal of sulphur. *Bismuth* cannot be removed by any metallurgical process applicable in residue or scrap melting oper-

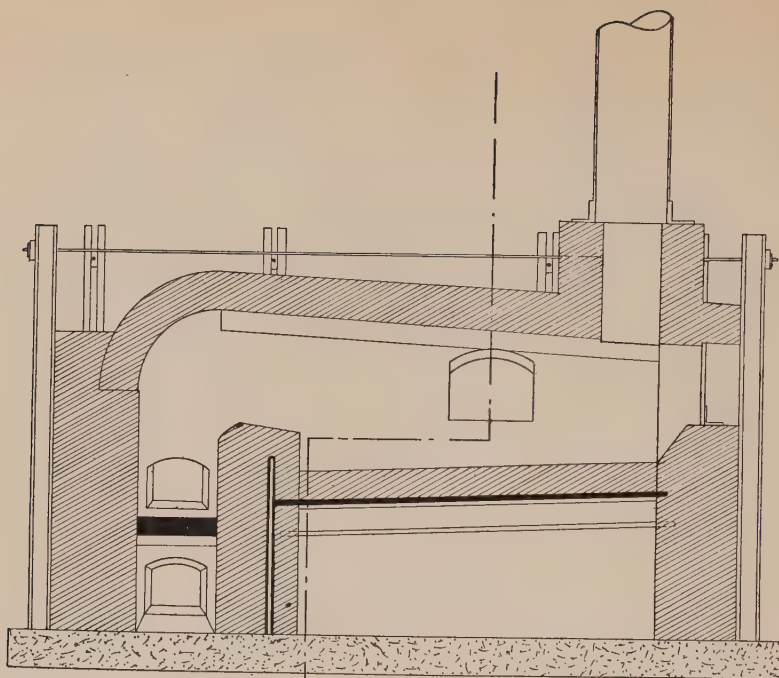


FIG. 11.

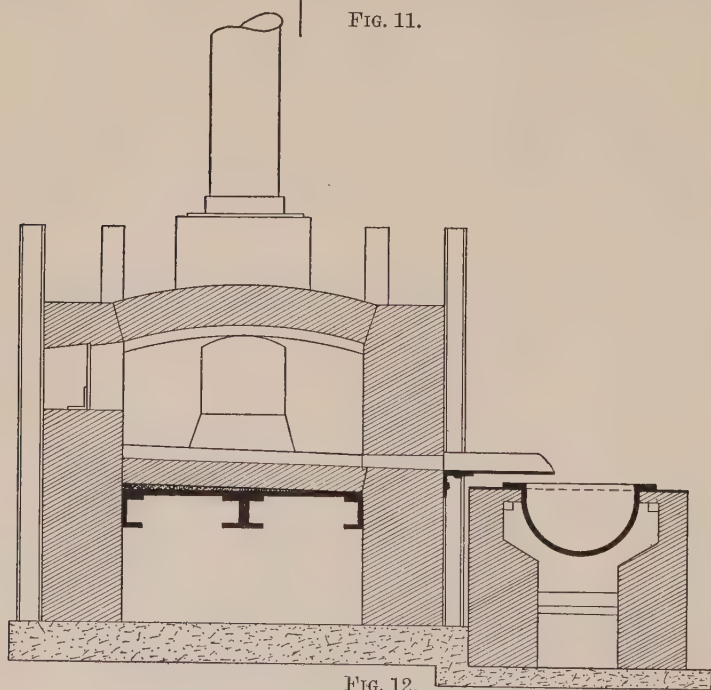


FIG. 12.

FIGS. 11 AND 12.—LIQUATING FURNACE.

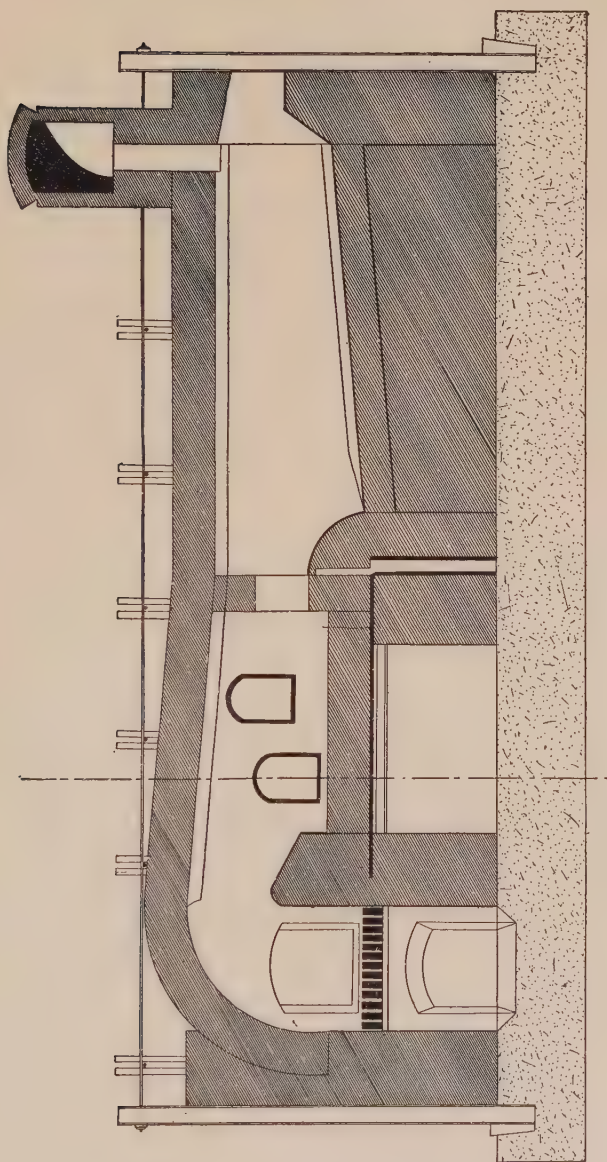


FIG. 13.—COMBINED DISTILLATION AND LIQUATING FURNACE.

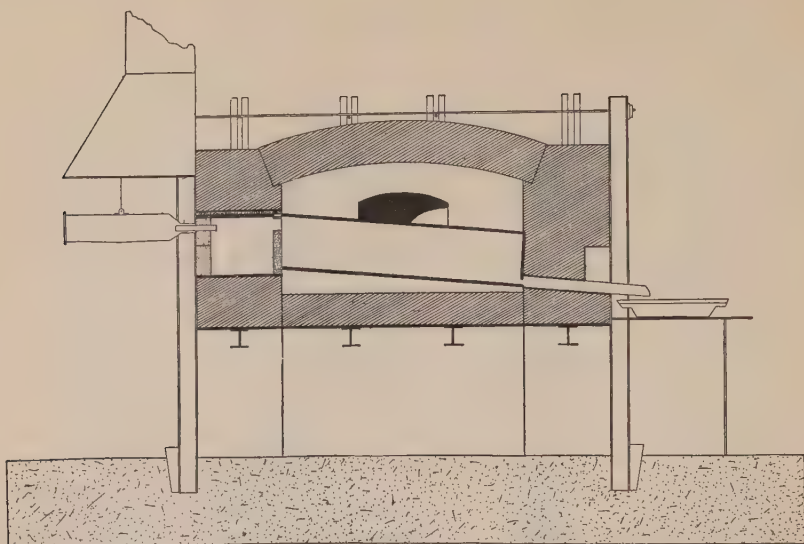


FIG. 14.—COMBINED DISTILLATION AND LIQUATING FURNACE.

ations, but since small amounts of this element do not exert any harmful effects in any of the groups of white metals, it is rarely considered, or even determined. *Cadmium*, which may be introduced into the general mixture by a number of alloys, reacts very much like zinc and is removed along with this element.

It is obvious that, while based upon identical principles, the methods used for the elimination of the various impurities from large quantities of metal are bound to differ more or less from those employed for the treatment of small quantities of scrap or raw secondary metals. And it is equally certain that, irrespective of the methods applied in either case, the treatment of large quantities of metal will give more satisfactory results, economically and technically, than that of smaller lots. While, on one side, the time, labor and fuel required in treating large bulks of metal must of necessity be less considerable if considered per unit of metal treated, metallurgical reactions are much more perfect and complete, and the ashes and drosses or similar by-products produced represent a much smaller percentage of the metal treated, than with smaller quantities of raw materials.

The complete preliminary refining treatment of large quantities of white metal scrap and secondary ingot metal (obtained from smelting

metallurgical and chemical residues in blast or reverberatory furnaces) is usually carried out as follows:

Copper (Iron, Nickel).—These elements may be eliminated by the segregation or the liquation process, the choice of which depends upon the presence of zinc in the material treated. Scrap- and secondary ingot metal free from zinc is best decopperized by liquation. Since in presence of larger percentages of copper, this process permits of a much more perfect elimination of this element than the segregation, or drossing, method, it is also used frequently even if the raw material proves to be decidedly zincish. The decopperizing action of zinc is effective with either method, of course.

The liquation process is carried out by subjecting a charge of white metal scrap or ingots, piled up at the cooler end of the furnace, that is to say, at the upper end of the hearth, to a gradually rising temperature, the original temperature being about 400° Fahr. It is obvious that this process may be carried as far as desired, the first half or three quarters of the total amount of the raw material liquated out being very poor in copper. As a rule, the copper contents of the first liquation products obtained from an original material containing from 3 to 8 per cent copper do not exceed 0.2 per cent, while in the presence of zinc or sulphur (nickel) this final percentage may be reduced to less than 0.10 per cent.

If a material containing considerable percentages of copper, tin, and antimony is subjected to this process, the hard dross containing the bulk of the copper will also retain a very considerable percentage of antimony and tin although the tin contents are concentrated in the soft metal. This partial separation of the constituents of the white metal is due, of course, to the different melting points of the various constituents of the heterogeneous alloys, the melting point of the eutectic, containing 56 per cent tin, 3.6 per cent antimony and 40.4 per cent lead being about 184° C.

If, on the other hand, the tin contents of the raw material subjected to liquation is higher than that of the eutectic, this will be concentrated in the second product, although in this case the tin contents of the eutectic alloy will be higher by a few per cent.

If the liquation temperatures are raised high enough, a very refractory material, consisting chiefly of copper, antimony and tin, and containing from 3 to 10 per cent of lead is obtained, which cannot be further treated in furnaces of the lighter type.

While qualitatively, the liquation process is more advantageous

than the segregation method in that the liquated metal is decopperized to a higher degree, it possesses a number of disadvantages, chief of which are the small capacity of even larger types of liquation units and the inability to entirely eliminate the zinc. Appreciable amounts of arsenic are only removed, or concentrated in the residues, if the raw materials contain larger percentages of iron.

Much better results are obtained by the segregation process, carried out in heavy reverberatory furnaces constructed so as to permit the formation of a comparatively deep bath of metal. Since during the last stages of the process the furnace charges are subjected to rather high temperatures, the depth of the hearth is limited by the height of the firebridge if coal or coke are being used as fuel, while in gas or oil fired furnaces the hearth may be made as deep as that of the tin-alloy furnaces (see page 150). It is obvious, of course, that the degree of separation is directly proportional to the depth of the hearth.

The Reverberatory Method of Refining.—Before charging the white metal scrap and ingots, the furnace is preheated at light red heat for at least three hours, or until the entire furnace is soaked full with heat; this will prevent possible freezing of the white metal from the bottom up during the second stage of the process. In charging the raw material, ingots and scrap containing comparatively small percentages of lead, and possessing the highest melting points, are charged first. Alloys rich in tin are not charged until the bath already formed is deep enough to take up the solid shapes, thus preventing unnecessary oxidation of valuable tin. It need hardly be pointed out here, that this difference in tin contents cannot be very high in any case, since the mixing of alloys rich and poor in tin will hardly be considered good policy by metallurgists. If for special reasons rich alloys must be added to metal poorer in tin, in order to obtain a certain tin content, this should be postponed until the different alloys have been subjected to the preliminary refining treatment.

The temperature to which the metal bath is to be raised depends on whether or not zinc or arsenic are present in the mixture. If both are absent, the metal is simply brought to a free melt, and firing discontinued, the temperature of the furnace and the bath being permitted to cool off gradually.

The same procedure may be followed if the metal contains comparatively large amounts of zinc since, as has been mentioned before,

zinc and copper possess a high degree of affinity for each other which causes them to separate out more perfectly than if copper was present alone. And since the crust formed is afterwards heated to very high temperatures, the bulk of the zinc is oxidized and rendered harmless without causing too large a loss of tin by oxidation, as would be the case if considerable percentages of zinc are eliminated by flapping.

If arsenic is present and the amount of zinc does not exceed a few tenths of a per cent, the metal is first brought to cherry red heat, and washed with thin-walled iron scrap such as wire, sheet scrap, etc. The arsenic forms an infusible compound with some of the iron, which is eliminated as dross. Most of the zinc present is also removed by oxidation, the rest of this element being oxidized by flapping at the cherry red heat, which is continued until the white zinc fumes cease to be emitted.

If sulphur is present in the metal, this is also eliminated at the same time, part of it forming a sulphide with the iron, while the remaining traces are eliminated by oxidation along with the zinc.

After the complete removal of zinc, arsenic, and sulphur has been made reasonably certain, firing is discontinued. The surface of the bath is skimmed clean, and all furnace doors opened wide to lower the temperature of the metal as rapidly as possible. If compressed air is available, a strong current of air may be directed into the furnace to assist in the rapid cooling of the metal, which is covered with a heavy cover of charcoal. The formation of a viscous layer of dross commences while the bath is still at a dark red heat. It grows in thickness and hardness until it becomes too hard to be penetrated with an iron rod, and it is the penetrability of a crust by an iron rod which is usually employed as a means of control of the progress of the cooling process.

The exact point at which segregation is to be discontinued by tapping the lower layer of fluid metal depends, of course, on the amount of copper present in the alloy, but for ordinary purposes it is generally considered advisable to tap when the iron rod is just able to penetrate the copper crust.

There are a number of tapping methods in use, the most common practice with furnaces of large capacity being to run the metal directly into slag dumping cars where it is permitted to cool off. The heavy lugs of white metal are then charged into other reverberatory furnaces, or into large melting pots, to be finish-treated. The chief dis-

advantage of this method lies in the fact that on account of the excessive weight of the white metal cones, a number of strong men are required to lift them into the furnaces. Since only a few of them can be charged at a time, most of the metal must thus be lifted into the furnace at red heat, an operation which, even with the more or less effective help of a block and tackle arrangement, is tedious and inefficient. Charging the heavy cones of metal into melting pots represents a still more difficult proposition, and many smelting works avoid the excessive strain on the pots and the almost unavoidable danger of splashing by remelting the cones in reverberatory furnaces and casting the metal into ingots of normal size.

It is obvious that all this trouble may be avoided by equipping the segregation furnaces with sufficiently large forehearth, the capacity of which should approximate at least half that of the furnaces. Previous to tapping a large number of ingot molds are placed in line around the pot, two or three rows of molds being placed above each other in such a way as to expose one half of the lower molds. Three or four good men are then held ready with well preheated ladles, and as soon as the metal begins to flow, it is ladled out of the pot and into the molds. Since this work is carried out by a number of men, the pot is rarely filled up completely, even if the metal pours out of the furnace in a heavy stream. If for some extraordinary reason the pot is filled before the furnace is emptied of white metal, the pressure of the metal has become low enough to render the closing of the tap a comparatively easy matter.

There is practically no spilling of metal, as is unavoidable if slag cars are being used, and since in the latter case each car requires the services of two men, one man tending the tap, and two other men fetching empty cars and emptying cold pots, the number of men required is considerably higher than if the metal is ladled from out forehearth. This difference is further accentuated by the fact that in recharging the ingots into furnaces or pots, only two men are required, who are able to charge the material much faster and more efficiently than the four or five men required to lift the heavy cones of metal into the charging doors.

Apart from the difference in the number of hands required, there is a world of difference in the ease of operation of the two tapping methods. Any one who has witnessed the excitement invariably connected with the tapping of large quantities of white metal into slag cars, and the splashing of hot streams of metal whenever a full car

is pulled away and an empty one pushed into place—usually through small lakes and rivulets of white metal—will appreciate the comparative ease and quietness with which the metal is ladled from forehearths.

If it is desired to subject the white metal to a further liquation process, it is obvious that best results can be obtained only with ingots, where the entire bulk of the charge is subjected to a uniform heat.

A further saving of time and labor is effected if the white metal obtained is to be finish-treated directly in melting pots, since the full charge of metal remaining in the forehearth after emptying the furnace may be further decopperized and purified directly. However, if the hard crust remaining in the furnace is to be liquated—as is usually the case—the melting pot must be emptied in order to make place for the second white metal. This difficulty may easily be eliminated, of course, by supplying the reverberatory furnace with a forehearth on both long sides, a large one for the first metal, and a considerably smaller one for the various products of liquation. The exact position of the two pots is to be carefully chosen, of course, since they must not interfere with the necessary operations. Both pots must be heatable, even though this consideration increases the difficulty of placing them in convenient position. Oil- or gas-fired furnaces are best suited for this purpose.

Treatment of the Crust.—The bulk of the first crust obtained consists of good white metal, a large percentage of which may be recovered by liquation. Since the first components of the original white metal bath to crystallize out are comparatively rich in antimony (PbSb crystals), the white metal remaining in the crust is richer in antimony and correspondingly poorer in tin, although this difference is not very much in evidence in the first liquation product if the furnace temperatures are raised sufficiently gradual. The same is true of the copper contents, which in the first liquation product are rarely higher than in the first white metal tapped.

Liquation may be carried out with open or closed tap hole. While under similar working conditions there appears to be very little difference of efficiency between the two methods, such a difference may be induced by the state of the crust material in the furnace. Thus, if the cooling process has been carried to a point where the crust has become a solid, or practically solid, lump, remaining spread over the full length of the hearth during the first stage of the liquating period,

liquating should be effected with the tap open in order to prevent washing out loose hard material on tapping. However, if the crust is just hard and stiff enough to be worked over and piled up at one end of the hearth, the tap may be closed between the various tapping intervals. The author has found that little is gained by working with closed tap, and that operations are much better controlled if the liquated metal is permitted to leave the furnace as soon as formed, being collected in the melting pot serving as forehearth. The tap is then closed for short periods only when, in order to separate the various qualities of liquated metal, the combined product of one liquating period is ladled out of the pot. As soon as the pot has been emptied, the tap is reopened and liquation continued at somewhat higher temperatures. Freezing of the tap may be prevented by directing a gas flame against and into the tap hole.

If the physical condition of the crust does not permit its collection at one end of the hearth at the beginning of the liquation period, it will be sufficiently soft to be scraped together after the first liquation product has been extracted, and since the efficiency of the liquation process is bound to be improved by this operation, it should not be deferred any longer than necessary.

The quantity of material representing the various liquation products is determined by the composition of the original white metal, the size of the crust, and by the different economical considerations prevailing in every individual instance.

If it is possible to regulate the heat so as to maintain certain temperatures, the best plan is to base the quantity of the different products on the respective melting points. For instance, the first liquation product may be considered all that part of the charge liquating out at a temperature of 375° Fahr., the second product may include all the metal liquating out at 400° Fahr. The third group should have a larger range of temperature, say from 400 to 475° Fahr., while the last soft product of liquation may be considered all the rest of the metal leaving the residue at temperatures of up to dark red heat. Each of these groups is ladled out and stored separately and used according to requirements. The last product is too high in copper, as a rule, to be directly used for alloying purposes, but may be decopperized to a high degree by being subjected to a liquation process at rising temperatures.

The hard residue of the liquation process is scraped out of the furnace and stored away, together with similar material, until enough

hard material has been collected to make a full charge. If this is not too hard and refractory, it is melted down and the bath cooled to a temperature of about 900° Fahr. when, on tapping, a considerable quantity of white metal is recovered. The residual material is then subjected to steadily rising temperatures until at medium red heat the tap is closed and the metal fused. If it is found that the lead contents of the fused residues are sufficiently poor in lead to be used as base alloy in the production of tin-antimony-copper alloys, it is then tapped and cast into small molds, although in the majority of smelters, this product, generally called "white matte," is treated for the separation of copper and iron from the white metal constituents.

Treatment of White Matte.—Apart from the electrolytic process, which is now being tried out with more or less success by a number of large smelters, the only established process of separation is that based on the sulphurization of the copper, which may be effected in the blast furnace or reverberatory, the former being the more efficient melting apparatus for this purpose. The blast furnace process is carried out as follows: The residues are smelted with fusible slag not too rich in iron, coarse coke—to speed up the smelting process—and a sulphurizing agent, the choice of which depends upon individual circumstances. As a rule, antimony or lead sulphide ores are used for this purpose, galena being the sulphurizing agent most commonly employed. Iron sulphide material must be kept out of the material, since if this cannot get oxygen, it will not give its sulphur off to copper. Metallic iron, or iron oxide, on the other hand, having a greater affinity for sulphur than copper, acts as desulphurizer and must also be kept out of the charge. The same is true of zinc. The larger the percentages of iron and zinc in the charge, the more copper will therefore be found in the white metal.

Apart from the sulphides, a certain amount of sulphate of lead may also be used as sulphurizer, although this should be ground with coal in order to make sure of its reduction to lead sulphide.

In order to attain as high a degree of sulphurization as possible and to prevent iron from being reduced out of the slag, the blast furnace must be worked comparatively rapid. Coarse coke is used and a strong blast maintained, while the fluidity of the slag is assured by adding fluorspar to the charges.

The bulk of the antimony goes into the white metal, while some of it is volatilized as oxide and sulphide. Since antimony sulphide is

readily volatile, very little of this compound passes into the matte. Small amounts of arsenic are eliminated by volatilization, while if this element is present in larger quantities, part of this will pass into the white metal.

The amount of tin and lead passing into the matte—which is always considerable—depends upon the degree of sulphurization of the charges. The larger the quantities of free sulphur available, the more tin and lead will be sulphurized along with the copper and iron. The chief consideration governing the efficiency of the process, meaning the production of as large a quantity of white metal poor in copper as possible, is therefore to control the sulphur contents of the charges so as to effect the sulphurization of the highest possible percentage of copper without carrying too large a proportion of the white metal constituents into the matte. The proportion of the amount of tin sulphurized to that of lead is determined by the considerably stronger affinity of lead for sulphur, so that the relative percentage of tin found in the matte will usually be found to be much smaller than that passing into the white metal produced.

The matte formed in this process contains from 20 to 25 per cent copper, and from 25 to 35 per cent, or more, lead, and this should then be subjected to a partial replacement process in the reverberatory furnace.

Treatment of the First Matte.—The purpose of this process is to replace the white metals contained in the first matte by another metal possessing a stronger affinity for sulphur than these elements. Copper and iron may be used for this purpose, but while more white metal is doubtlessly liberated by iron, the first matte is usually treated with copper in the first place in order to avoid too high a degree of contamination of the matte with iron.

The charge is therefore made up of crushed matte, enough copper oxide to correspond to about 50 per cent of the copper present in the matte, 5 to 10 shovels of reducing coal, and an approximately equal amount of crude sodium sulphide—generally known as black cake.

The melting process is carried out at a moderate red heat.

The products of this preliminary treatment of the first matte are impure lead, containing some tin and copper, and second matte, containing from 30 to 35 per cent copper.

The matte is then subjected to a similar smelting treatment in the reverberatory furnace, using iron oxide instead of copper oxide.

The success of this treatment, which, as a rule, is the final treatment effected within the smelter, the matte produced being sold to other smelters, is solely dependent on the correct quantity of iron added to the charge, but it is practically impossible to separate all the white metal from the leady matte without forcing a considerable percentage of copper into this product.

Treatment of the White Metals Obtained from the Replacement Processes.—It is obvious that the three white metal products obtained from the smelting treatments of the matte are of widely differing composition. The tin contents of the first white metal produced in the blast furnace treatment of the original white matte is considerably higher than that of the third product, which, as a rule, is higher in copper than the first two grades of white metal obtained. The percentages of arsenic decreases with the tin contents, comparatively large amounts of this element volatilizing at each smelting treatment involving higher temperatures and the presence of an excess of sulphur.

As a rule, all these products are added to white metal scrap or impure ingots of secondary metal to be subjected to the preliminary refining process in the reverberatory furnace.

Final Treatment of Reverberatory-Refined White Metal Alloys.—While the reverberatory treatment of refining white metal is very efficient in removing excessive quantities of impurities from raw scrap or blast furnace ingots, it is economically impossible to effect a sufficiently high degree of refining to render the product marketable, unless the raw materials used are of unusual purity. In the latter case, the purpose of efficiency is better served if the pure scrap or secondary ingot metal are refined directly in the melting pot.

The principles underlying the elimination of the various impurities by the melting pot methods are identical with those governing the reverberatory process, modified to suit the specific conditions of the smaller and externally heated unit.

The removal of the copper is carried out as follows: The white metal is charged and melted down in the pot until this is filled up to within 5 inches from the top; it is then mixed thoroughly, firing is discontinued and the metal allowed to cool off gradually. With decreasing temperatures, a dark viscous dross begins to separate out on the surface of the metal, which gradually hardens. As soon as this layer has attained a thickness of about $\frac{1}{2}$ inch, it is taken off by means of perforated ladles, which permits the soft white metal

entrained in the dross to drain out, leaving behind a dry, crystalline mass containing the bulk of the copper present in the melt. The percentage of copper contained in this dross depends on the amount of copper present in the metal and on the thickness of the crust, and may vary from 2 to as high as 10 per cent, although the latter figure is only attained if in treating very coppery white metal, the drossing and taking-off temperatures happen to be very high. It is not necessary, of course, to cool the melt down to near freezing temperature, since with higher percentages of copper, this will form a dross at temperatures as high as 450° C. (850° Fahr.), although small percentages, such as 0.25 per cent, require a much lower temperature to form a satisfactorily comprehensive dross. By this process the percentage of copper may be reduced to about 0.10 per cent with low tin alloys, but to not less than 0.18 to 0.20 per cent if the metal contains a high percentage of tin. If it is desired to lower the percentage of copper in the white metal alloy still further, the metal must be subjected to the sulphurizing process.

The old sulphurizing process which, as usually carried out, consists of throwing a few pieces of lump sulphur or sulphur sticks on the surface of the bath, stirring the metal vigorously to obtain as high a degree of sulphurization of the copper as possible before all the sulphur has been burned off, is decidedly faulty. It appears obvious that since only a small proportion of the fused sulphur and practically none of the vaporized sulphur is utilized for sulphurization proper, only a small percentage of the copper remaining in the white metal after drossing can be eliminated by this process. The most efficient simple process of sulphurization, using elementary sulphur as reagent, is the following:

After removing the bulk of the copper separated by segregation, the contents of the pot are heated to a temperature of about 850° Fahr. A few pieces of lump sulphur or sulphur sticks in a sulphurizing box are then brought down as far as possible below the surface of the metal. The sulphur is vaporized, and the vapor generated stirs up the metal thoroughly, thus effecting the intimate contact between the copper contents of the metal with the sulphur required to attain a maximum degree of sulphurization. A large part of the copper combines with the sulphur, forming copper sulphide, which rises to the surface of the metal, where it is removed together with the white metal dross formed. The attempt to increase the reactive capacity of the sulphur by the addition of a few pieces of potatoes or similar

material to the sulphur charge in the box, while correct in theory, is practically useless, since the exceedingly small amounts of water vapor produced cannot possibly have a noticeable influence on the success of the sulphurizing treatment of several tons of metal.

The sulphurizing apparatus consists of a square or cylindrical iron or steel box, about 5 to 7 inches long and from 3 to 5 inches wide, welded on to an iron rod at least 7 feet long. This rod should be made as long and as heavy as possible since the back thrust created by the specific gravity of the bath and the vaporization of the sulphur renders the operation of a light rod exceedingly difficult. The lid of the box, which should be turned downward, is perforated for the escape of the sulphur vapors. Since at the high temperatures of the process the walls of the melting pot are severely attacked by the sulphur vapors, the sulphurizing box should not be welded to the extreme end of the rod, but about 4 or 5 inches from the point, so that on resting the rod on the bottom of the pot, the sulphur vapors will not reach the bottom.

The dross obtained, which contains only a very small percentage of copper, or copper sulphide, may be added to a reverberatory charge of white metal. Although theoretically the introduction of sulphur or sulphides at that early stage of the decopperizing process does not appear to be good practice, the very small quantities of sulphur contained in the dross are unable to influence the process either way. If large quantities of this material are produced, blast furnace treatment is to be preferred.

Next in order of removal is the zinc. If the white metal has previously been subjected to a reverberatory refining process, zinc is only present in traces, especially after a sulphurization treatment of the white metal bath for copper. Indeed, it appears practically impossible that any zinc should remain in the white metal, unless this has been introduced later, since in liquating or drossing copper as well as in sulphurizing the metal, strong influences are also exerted on the zinc. It is not generally known that the affinity of zinc for sulphur is as strong, or perhaps stronger, than that of iron, and noticeably stronger than that of copper for sulphur, so that if considerable percentages of zinc are present in white metal, less copper is sulphurized by the volatilization of a certain amount of sulphur than with non-zincish material, since a large percentage of the zinc is removed along with the iron.

Small amounts of zinc are removed by steaming, since apart from

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the fact that this element is removed just as easily by oxidation, steaming has a general refining action on the metal, while sulphurization requires a consequent steaming treatment to remove the small amounts of sulphur, or sulphides, remaining in the melt. The use of boiler steam is not to be recommended for this purpose, however, even if highly superheated, since on account of the formation of water of condensation in long and thin transmission pipes, serious explosions may be caused.

This danger is avoided in a very simple and effective manner by using the steaming appliance sketched in Figure 15, which, besides

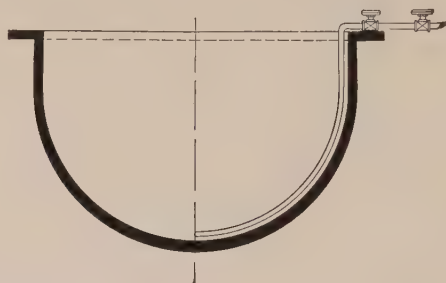


FIG. 15.—STEAMING APPLIANCE FOR MELTING POTS.

being absolutely safe and very cheap in construction and operation, does away with the need of steam boilers or other costly and bulky apparatus.

One end of a seamless water pipe is bent so as to exactly fit the walls of the melting pot. The other end of the pipe is connected with the regular water supply system, the connection being secured by two valves. The handle of the valve nearest to the rim of the pot is removable and remains in the custody of the foreman, while the other valve is operated by the man in charge. If steam is required, the first valve is closed tightly and the other valve is then opened wide. The first valve is now opened as cautiously as possible until the metal commences to boil vigorously, and the handle removed in order to prevent irresponsible persons from fooling with the valve, which may cause violent explosions. Finally, the second valve is turned back until the surface of the bath is just seething.

The principle of this steaming process is obvious. By correctly regulating the two valves, but small quantities of water are permitted to enter the pipe at a time, which are immediately vaporized

by the heat of the metal, being forced through the bath, unless the water pressure in back of the pipe is not sufficiently strong to overcome the weight of the metal. However, since at a depth of the bath of 1 yard a white metal of a specific gravity of, say, 10 the pressure required would be equivalent to a head of only about 35 ft., no difficulties will ordinarily be experienced from this source.

The relative position of the various parts of the steaming device towards the water main must be such as to permit the individual drops of water to run straight down into the heated section of the pipe without forming pools at any part of the system. If the water is able to segregate at any one point, a slight disturbance of the position of the pipe may cause the whole amount of water collected to enter the hot section at once, giving rise to serious explosions.

For the removal of zinc or sulphur, steaming is usually carried out for about 10 minutes, when a sample is drawn and examined for surface appearance, fracture, etc. If satisfactory, the metal is then ladled out, while if the sample still indicates the presence of zinc, or sulphur, steaming is continued some three minutes longer.

Other Refining Methods.—The refining of white metal alloys is still frequently carried out by forcing compressed air through the bath, or by washing treatments with hydrochloric acid or inorganic chlorides. None of these methods gives as good results as the steaming process. While quantitatively the oxidizing effect of air on the impurities equals that of steam, it possesses a very strong oxidizing action on tin and antimony, thus giving rise to considerably higher losses of these elements than steam, especially if the air treatment is permitted to continue for any considerable length of time.

Hydrochloric acid, besides influencing but weakly the impurities of the white metal alloys, has a serious corrosive influence upon the iron and steel parts of the melting pot plant, particularly on the hood, which quite frequently is completely destroyed within a month or two. If salammoniae (ammonium chloride) is used instead of hydrochloric acid, corrosion of the iron parts is avoided, but the refining effect of this reagent is not much better. It has been pointed out already that cleaning methods based upon the covering of the metallic surface with the reagents in question can only be of secondary importance, especially, if as is the case with hydrochloric acid and most of the chlorides, this reagent volatilizes too rapidly to permit of a perfect and sufficiently thorough contact of all the metal with the reagent. Only where perfectly clean alloys, such as soft

solders, etc., are being poured at comparatively low temperatures, the occasional addition of salammoniac or typical white metal fluxes such as resin or certain fats, will yield beneficial results in maintaining a bright and clean surface free from oxides.

The removal of arsenic from white metal in melting pots is practically impossible, since boiling with steam as well as sulphurizing or the application of fluxes will lead to excessive loss of tin. A small part of the arsenic present may be removed by washing with caustic soda.

Whatever the various refining treatments applied, casting of the white metal should always be preceded by a short steaming period in order to remove the last traces of the refining agent used. This applies particularly if the sulphurizing treatment has been employed, a period of steaming of from 5 to 10 minutes being sufficient for this purpose.

Removal of Antimony.—One of the most important and difficult problems connected with the melting treatment of white metal scrap and the separation of undesirable components is the partial or complete removal of antimony. Since this element alloys with tin and lead in practically all proportions, it cannot be made to settle out like copper and iron, while its affinity for oxygen does not distinguish this element sufficiently from tin and lead to permit its removal by means of boiling with steam or air without at the same time oxidizing practically all of the tin.

The various other processes suggested, such as mechanical filtration of crystals from a semi-solid mixture of the components, or centrifuging, are not satisfactory from a practical point of view, since they cannot be worked on a sufficiently large scale to justify application under practical works conditions. Fractional crystallization, the only exception to the rule, does not reduce the antimony contents of the common white bearing metal alloys to less than 3.7 per cent, which represents the inseparable part of the eutectic of the ternary lead-tin-antimony alloys. However, since this process represents a valuable mechanical means of separating common bearing metal alloys into fractions ranging from very high to low antimony contents, it may prove useful as a preliminary method for the removal of antimony wherever the antimony contents are too high for economical application of the other methods in question. It should be pointed out in this connection that the same principle of fractional crystal-

lization is applied in the production of "Tin-Alloy" from bearing metals which will be discussed in the following chapter.

Fractional crystallization as applied to the ternary lead-tin-antimony alloys proceeds as follows: On cooling the fused alloy containing more or less copper gradually, dendritic crystals holding from 30 to 40 per cent copper are first crystallized out. According to Heyn and Bauer,¹ these may be regarded as representing mixed crystals of copper and tin containing considerable percentages of lead and antimony. In relatively thin layers, as for instance in bearing shells, these crystals form a lattice system throughout the whole mass of metal, thus preventing the segregation of antimony. However, if the cooling of the alloy is carried out in deep containers, such as melting pots, the separated copper crystals rise to the surface, gradually forming a hard dark crust. In practical smelter work this crust is usually taken off and subjected to a liquation process leading to the production of white matte and hard white metal.

The first true white metal crystals forming after the separation of the copper alloy crystals solidify at temperatures of from 240 to 590° C. depending upon the percentage of antimony present. These crystals are very rich in antimony. Some of the "antimony cubes" separated by Heyn and Bauer contained 50.4 per cent antimony, 43.5 per cent tin, and 5.3 per cent copper. If the melt is allowed to stand quietly, the crystals rise to the top, so that the upper layers of the bath become enriched in antimony and copper, while the tin is concentrated in the liquid portion. The final temperature of the process ranges from 182 to 185° C., at which point the eutectic, containing 55 per cent tin, 3.5 to 3.7 per cent antimony, and 0.1 to 0.2 per cent copper (rest lead) commences to crystallize. This critical temperature may sometimes be lowered by under-cooling phenomena, which in the case of the lead-tin-antimony alloys are often quite pronounced.

This process may be carried out in melting pots as well as in reverberatory furnaces. If the object is to reduce the antimony contents of the alloy to a percentage which permits the application of one of the other processes for the complete elimination of this element, it may be carried out in melting pots, while the reverberatory furnace method is usually employed for the production of "Tin Alloy." (Page 145.)

The melting pot process is manipulated as follows:

¹ Mitteilungen a.d. Materialpruefungsamt, 1911, p. 29.

The melting pot is charged with bearing metal scrap until it is filled with molten metal. The fire-box is then emptied and this as well as the ash pit are tightly closed to prevent too rapid a cooling of the bottom of the pot. The first product formed is the copper crust which is removed and treated for the production of white matte. On reaching a temperature of about 250° C. (about 500° Fahr.) crystallization of the white metal commences, the crystals being taken off as rapidly as formed. As the temperature of the bath reaches 200° C. (400° Fahr.), crystallization proceeds quite rapidly, and it becomes necessary, to work the skimmer downwards along the walls of the pot to remove the crystals forming on the cooled surfaces. At a temperature of approximately 187 to 186° C. (370 to 367° Fahr.) the liquid portion of the charge contains about 4.00 to 4.20 per cent antimony, which may then be removed by one of the other methods.

If it is desired to reduce the antimony contents of the bath to the lowest possible percentage attainable by this method, crystallization is continued until the metal bath has reached a temperature of about 184 to 183° C. (363 to 365° Fahr.), when the rate of crystallization rapidly decreases until it ceases entirely for a few minutes. This point indicates the beginning of the crystallization of the eutectic alloy. The remaining liquid melt must now be ladled out as quickly as possible since crystallization of the eutectic proceeds rather rapidly.

The progress of this process need not necessarily be followed by measuring the decreasing temperature; it may also be judged very accurately by observing the crystallization phenomena taking place at the surface of the metal. Following the period of copious crystallization, the crystals formed begin to increase in size until, finally, they appear as large, jagged skins of crystalline shape which on being lifted out of the metal behave like heavy scales. The gradual disappearance of these crystals indicates the rapid approach of the eutectic composition of the remaining melt, and as soon as the surface of the bath remains absolutely clear for a short time, the liquid metal must be ladled out with all possible haste.

Since the crystals skimmed off the surface of the bath decrease in antimony and increase in tin until the final point has been reached, it is necessary to separate them into three or four equal lots to be remelted and treated separately.

The process described is not recommended for the production of the final eutectic unless the capacity of the pot exceeds 15,000 to

20,000 pounds and provided the tin contents of the original alloy exceed 45%, while if it is desired to produce an alloy containing about 4.2 per cent antimony, the capacity of the pot should not be less than 10,000 pounds, at a tin content of the original alloy of at least 40%. The production of Tin-Alloy is most efficiently carried out by the methods discussed in the separate chapter on this subject.

REMOVAL OF ANTIMONY BY OTHER PROCESSES

In view of the fact that on account of the perfect solubility of antimony in white metals complete elimination of this metal cannot be effected by physical or mechanical means, modern research work is almost exclusively directed towards the removal of antimony from white metal alloys by addition of some other metallic or non-metallic elements possessing a pronounced affinity for antimony which tend to take up this metal by forming drosses or specifically lighter alloys.

One of the oldest methods suggested for this purpose is based upon the close metallurgical relationship between antimony and *arsenic*. The most well known and generally applied method of removal of arsenic from white metals is the treatment of the red hot alloy with iron or some other metal of the iron group. Louis¹ was able to show that hard tin crusts containing large percentages of iron may take up as much as 25 per cent of arsenic, and that the percentual proportion of such a tin-arsenic-iron mixture may be as 1:1:2, proving that 50 per cent of the tin contents of the hard tin crusts may be replaced by arsenic. In view of the similar metallurgical behavior of arsenic and antimony, treatment with iron or similar metals should therefore tend to effect the more or less complete elimination of antimony also.

Experiments carried out along similar lines by treating impure tin containing larger percentages of antimony with artificial tin crusts composed of equal parts of iron and tin at temperatures of above 1800° Fahr. and subjecting the resulting mixture to a liquating treatment proved the impracticability of this method. On liquating, the raw mixtures released only relatively small percentages of tin, and it was found necessary to effect a better mechanical separation by pressing the liquid portion of the mixture through a narrow-meshed sieve at a temperature of about 1200° Fahr. The hard tin crust, containing 50 per cent of iron did not take up more than 10

¹ Louis, *Metallurgy of Tin*, 1911, pp. 6, 7.

per cent antimony, so that if large amounts of this metal are to be removed excessive quantities of tin crust would have to be used to effect satisfactory separation. Thus, if 1000 pounds of hard tin crust, containing 50 per cent iron, are added to 20 tons of white metal, containing 4 per cent antimony, only 100 pounds of antimony, representing 0.5 per cent of the antimony contents, are actually removed. These 1000 pounds of crust, on the other hand, would form a dross at least five times this quantity, so that, apart from the small amount of antimony removed from the white metal, this process would necessitate the treatment of excessive quantities of drosses, especially if enough hard tin crust is added to the white metal to effect the elimination of at least 50 per cent of the antimony present. Thus it appears that at the present state of development this process is useless for all practical purposes.

Experiments with the other members of the iron group are being made in a number of smelters but did not yield much better results.

The only exception to this rule appears to be *aluminum* which, if added in correct proportions and under suitable conditions, effects a practically quantitative elimination of aluminum from white metals. Theoretically 1 part of aluminum combines with 2 parts of antimony, and if the process is carried out with due attention to the metallurgical principles involved, all but about 0.10 per cent of antimony may be removed. If the original amount of antimony contained in the white metal alloy is known and if exactly half of this quantity of aluminum is added, the percentage of aluminum left in the metallic bath will be twice that of the remaining percentage of antimony. The amount of dross formed is not excessive, and its treatment does not offer serious difficulties, best results being obtained in the reverberatory furnace.

The chief difficulties involved in the application of this process are due to the comparatively high melting point and the low specific weight of aluminum. A number of smelters introduce aluminum by stirring aluminum foil and similar material into the overheated white metal bath, while others prefer to add the aluminum in the molten state. Of these two methods the latter is by far the most efficient, provided a suitable melting appliance, such as a crucible furnace, is available to melt the aluminum required.

Before adding the aluminum, the white metal alloy should be heated to a temperature of at least 1100° Fahr. It is also advisable to add an equal amount of white metal to the aluminum before

charging this metal into the white metal bath. The mixture should be heated to about 1200° Fahr. in the crucible and poured out in a thin stream, stirring the white metal vigorously while adding the aluminum mixture and for at least 10 minutes afterwards. Perfect results are only obtainable if stirring is carried out mechanically. The white metal is then permitted to cool down until a thick dross has been formed, which is taken off to be liquated.

The small amounts of aluminum remaining in the white metal after drossing are removed by steaming the metal at a temperature of about 1100° Fahr. The dross is liquated at low temperatures to remove as much of soft white metal as possible. The residues are subjected to an oxidizing treatment in the reverberatory to remove metallic aluminum, or charged in the blast furnace where the aluminum is slagged.

Magnesium is another poor elimination agent for antimony, which is mainly due to the fact that the compound Sb_2Mg_3 , and the tin compound SnMg_2 also produced, form solid solutions. These solutions tend to form a eutectic with the rest of the white metal alloy, the two phases of which appear to be mixed crystals consisting of Sb_2Mg_3 and SnMg_2 and a mixed crystal of the system Sn-Sb rich in tin. While on subjecting the mixture to liquation, the former, possessing a comparatively high melting point, remain with the hard dross, the eutectic goes over with the liquated metal, so that a white metal free from antimony can never be obtained by this method.

Somewhat better results may be obtained with *the metals of the alkali and alkaline earth groups*, of which *metallic sodium* is a characteristic example. The concentration of a large percentage of the antimony present in white metals in a comparatively small amount of dross easily melted is one of the main advantages of this method, although its application to white metal alloys containing as high as 10 per cent of antimony, as has been advocated by some German authors, is absolutely impractical and uneconomical under actual working conditions. It is also impossible to remove more than 2 or 3 per cent of antimony at one time without causing more trouble of a contributory nature than the elimination of larger percentages may be worth.

The chief difficulty connected with this process is the exceedingly low melting and flaming temperature of sodium and the low specific weight of the metal. Thus, if the sodium is placed on the surface of a white metal melt it will flame up almost immediately. Even if

by frantic paddling some of the molten sodium is brought under the surface of the white metal, part of it is oxidized and rendered useless for the purpose in question. The rest of the sodium, if stirred in thoroughly, forms a dross with part of the antimony present, 1 unit of sodium combining with from 1 to $1\frac{1}{2}$ units of antimony. Trying to improve the stirring-in process by using mechanical stirring devices is bound to lead to failure since it is impossible to force the molten sodium into the white metal. Most of the burning sodium is collected in the apex of the vortice created by the stirrer, where it is completely oxidized.

Along with the NaSb compound formed, a certain percentage of NaSn is also produced, although the percentage of tin contained in the dross is rarely higher than that of the metal treated, while the tin contents of the latter are seldom changed, or if so, towards higher figures only. For instance, a white metal alloy containing 35 per cent tin and 4 per cent antimony will, after treating with 2 per cent of sodium and drossing, contain from 35.0 to 35.2 per cent tin and about 1.5 to 2 per cent antimony.

The amount of dross produced ranges from 15 to 25 per cent, depending upon the percentage of antimony to be eliminated, or on the amount of sodium added. If more than 2 per cent of sodium are added, the above figures for drossing may be considerably exceeded. On liquating, this dross yields about 50 per cent of metal and 50 per cent ashes, the percentage of antimony contained in the former ranging from 2 to 4 per cent, while the ashes may hold from 15 to 35 per cent antimony, depending on the liquating conditions maintained.

In view of the high degree of affinity of sodium for oxygen, it is obvious that the small amounts of sodium left in the white metal after drossing are removed without difficulty, and within a comparatively short time. As a rule, ten minutes of boiling will suffice to remove all traces of this element.

The handling of the drosses containing considerable amounts of sodium involves a number of disagreeable features due to the more or less rapid oxidation of the metallic sodium and the caustic properties of the oxidation products. On subjecting the drosses to the elevated liquation temperatures, they commence to glow and burn, although this phenomenon does not exert any deteriorative influence on the liquation process. The antimony contents of the liquated metal are not noticeably increased, unless carbon or some other

organic materials are also present, when the bulk of the antimony contents of the dross passes into the liquated metal, the antimony contents of the ashes being reduced to less than 10 per cent.

Numerous attempts have been made to enlist the well known affinity of *zinc* for antimony in this cause. It has been determined that the affinity of zinc for antimony is considerably stronger than that for tin, although, as a matter of course, a slight concentration of tin in the drosses is to be expected.

If this method is carried out so as to collect the antimony in a dross, the efficiency of the process is too low for practical purposes, the chief disadvantage of the zincing method being the contamination of the white metal with zinc. Decidedly better results are attained, however, if this process is combined with a liquation treatment when, apart from a partial concentration of the antimony in the residues, the tin contents of the original metal are not noticeably decreased. It is impossible even in this case, of course, to keep the liquated metal free from zinc, and since the elimination of appreciable quantities of this element from white metal alloy rich in tin causes a considerable loss of tin by oxidation, this process will hardly be introduced in practical operation. Experiments carried out by the author showed that the liquated metal contained as high as 0.6 per cent zinc, while the second, hard liquation product showed from 0.6 to 1.0 per cent of this metal. The elimination capacity of zinc is low, and it will be found difficult to remove more than 1.0 to 1.5 per cent antimony with an addition of 2 per cent zinc.

Of the various methods investigated with a view to their value in the elimination of antimony from white metals, *sulphurizing treatments* have taken a prominent place. However, in view of the fact that the affinity of antimony for sulphur is not nearly as strong as that of tin, or even lead, satisfactory results cannot be obtained with the sulphurizing treatment generally applied to white metals, unless the process is carried out for the purpose of separating larger percentages of tin and lead from the antimony which is thus concentrated in the residual metal, while the sulphide dross carries correspondingly larger percentages of tin. But since the quantities of sulphides produced are not nearly large enough to be economical and since, on the other hand, it is usually considered bad metallurgical practice to convert good metallic alloys into chemical compounds, this process is of theoretical interest only.

Different conditions obtain if the sulphurization process is carried

out with a view to volatilizing the antimony sulphide formed. There are three different methods by which this separation may, perhaps, be achieved, e.g. the blast furnace, reverberatory, and melting pot processes, all of which have been, and still are being investigated.

By the blast furnace method white metal ashes, slags, oxydic drosses, and similar materials are melted down with the requisite quantities of slag-forming materials and sufficient sulphidic additions to sulphurize the copper, tin and antimony present. It is then necessary to adjust the proportions of fuel, iron, and sulphidic materials, and the volume and pressure of the blast so as to sulphurize all the above indicated metals, copper and a certain percentage of tin and iron entering the matte, while the bulk of the tin and lead is finally reduced to metal and most of the antimony sulphide vaporized. If arsenic is present, part of the antimony will also go into the speise. The percentual amount of tin entering the matte may rather closely be regulated by adjusting the quantities of iron added to the charges. The effects of an excess of iron may be eliminated by regulating the volume of the blast so as to oxidize the excess.

Although some success is said to have been obtained with this method by a German smelter with raw materials containing 1 and 2 per cent antimony or less, it appears that in view of the considerable loss of tin by vaporization and matting, this process will never be of great practical importance, even if it is possible to develop the operating details to a point where the continuous close control of the furnace reactions is rendered unnecessary.

Similar conditions prevail in the case of the reverberatory process, where the white metal ashes and slags are subjected to a sulphurizing treatment at high temperatures, the three products obtained being a metal comparatively low in tin and antimony, a matte rich in tin and low in antimony, and slag low in tin, antimony and lead. Apart from the volatilization of the bulk of the antimony present, a large percentage of tin is also volatilized, rendering this process practically useless.

Attention may in this connection be called to another reverberatory process, by which the ashes containing from 1 to 4 per cent antimony may be subjected to heat and oxidation influences in such a way as to concentrate the bulk of the antimony in the dross.

For instance, if a lead ash, containing several per cent of tin and antimony, is charged into a reverberatory furnace at a temperature of about 1500° Fahr., and the furnace atmosphere is maintained

neutral, or slightly oxidizing—the only reducing agent being the 5 per cent charcoal or coke mixed with the ashes—the metal produced consists of about 99.5 per cent lead, rest antimony and a little tin.

If no tin is present, this process may be conducted so as to produce a metallic lead containing comparatively small percentages of antimony, and a dross, which on reduction will give a hard lead rich in antimony. The same results are obtained with antimony slags, which if melted down in a reverberatory furnace and mixed with from 5 to 10 per cent of coal or coke, give up a certain percentage of lead comparatively free from antimony, this element being concentrated in the slag. If the concentrated antimony slag is smelted in a blast furnace, it will yield an antimony lead containing from 12 to 20 per cent antimony.

The Tin-alloy Process.—The tin-alloy process permits of the separation of old bearing metal alloys into a number of alloys considerably richer and poorer in tin, antimony, and copper than the original alloy. The amount of tin-alloy thus produced may vary from 30 to 50 per cent of the original alloy treated, and this product represents a very desirable and comparatively pure base alloy for a large number of important industrial alloys. For certain purposes such as the production of white metal solders the antimony contents are generally considered too high, that is to say, too high to suit the trade, although this fact is in no way indicative of actual conditions. It is well known, for instance, that tin-alloy is employed as base alloy for the production of solder in practically all European countries, and it has been shown (Soft Solders, page 83) that a certain small percentage of antimony is actually of advantage for many purposes. However, since producers cannot force their convictions on the users of metallic alloys, it is necessary to decrease the antimony contents of the finished product either by dilution or by full or partial elimination of this element by metallurgical processes.

Since in the production of tin-alloy economical considerations demand the use of white metals of comparatively high tin contents, bearing metal scrap is almost exclusively used for this purpose, the removal of the comparatively large amounts of copper and antimony, as well as of the rarer constituents such as aluminum, zinc, etc., representing the chief problems to be solved by the metallurgist. The average percentages of copper and antimony present in bearing metals vary between 5 and 15 per cent, while those of zinc, if present, range from 0.10 to 3.0 per cent.

The first really efficient process for the elimination of impurities, and the production of tin-alloy from bearing metal scrap relatively poor in copper and antimony was devised in England, but the method employed was apparently unsuited to the production of pure grades of tin-alloy from bearing metals containing larger percentages of copper and antimony, so that on account of the purity of bearing metal alloys required, the alloys produced proved to be relatively expensive.

Theoretical Considerations.—The theoretical principles underlying the production of tin-alloy are comparatively simple. It is known that on gradually heating any lead tin-alloy, containing considerable percentages of tin, to 181 to 183° C., the alloy begins to "sweat," small drops of fused metal appearing at the surface of the metal. On raising the temperature of the alloy a few degrees above 183° C., sweating increases until all the constituents of the alloy rich in tin have been liquefied. The metal liquated at a temperature of about 182° C. is the eutectic of the lead tin-alloys, containing 63 per cent tin and 37 per cent lead, if the original alloy is free from impurities.

Quantitatively and qualitatively similar results may also be obtained by reversing the process, that is to say, by gradually cooling a liquid tin-lead alloy down to the melting range when, according to the melting curve diagram of the alloy, poor tin alloys will crystallize out first, the percentage of tin remaining in the melt increasing in proportion.

On reaching the freezing, or melting range, crystals relatively poor in tin commence to separate out on the bottom and at the walls of the container as well as on top of the metal, while the liquid portion of the melt is gradually approaching the eutectic composition. If, at the proper moment, the hard top layer of the metal is pierced, the eutectic alloy, tin-alloy, may be poured out. If the white metal alloys subjected to this process contain more than about 60 per cent tin, the reverse conditions prevail, the first metal to separate out being higher in tin than the eutectic. This method is sometimes used for the reduction of the lead contents of alloys containing 70 per cent tin or over. In practical operation, the critical temperature is indicated by an interruption of the uniform temperature decrease or, occasionally, if very sensitive heat measuring apparatus is being employed and if the tin contents of the original alloy are very high, by a momentary rise in temperature.

This method forms the basic principle of the modern tin-alloy

process which, being applied to the corresponding treatment of white bearing metals, is rather complicated by the impurities present. Apart from the purely contaminating character of these elements (copper and antimony) they possess the serious disadvantage that if the cooling process is not carried through properly, the crystallization and segregation of the copper-antimony alloy material will carry with it considerable amounts of valuable tin, while large quantities of copper will counteract the segregation of the solidified crystals. This fact is the reason for the addition of copper to bearing metals, where segregation of the antimony crystals must be retarded as much as possible of course.

It is a peculiar fact, however, that small percentages of copper are really required to obtain a satisfactory degree of separation, and it will be found by simple laboratory experiments that tin-lead-antimony alloys free from copper represent very poor raw materials for the production of tin-alloy. However, since by employing efficient methods and by working with deep layers of metal the elimination of copper may be carried as far as desired, and since small percentages of this metal exert a more or less mechanical influence only, the production of tin-alloy may be regarded as representing a process strictly typical of the ternary alloy lead-tin-antimony.

The ternary diagram, Figure 16, shows that melting and freezing conditions are considerably more complicated in the case of ternary alloys than in that of the corresponding binary alloys, the most striking difference being the presence of two well-defined eutectics, one of which solidifies at 185°C ., the other, at about 240°C .

The position of a ternary alloy of this type relative to these two eutectic points is in the first place determined by the percentages of tin contained, while the percentages of antimony—in the case of the common bearing metals—are of but relative importance.

While the liquefying or melting of crystals is accompanied by the absorption of a certain amount of heat, an equivalent amount of heat is set free if on cooling down, the crystals separate from the melt. Thus it is clear that with as gradual a decrease of temperature as is possible in a 10 or 15 ton furnace, the solidification of relatively large quantities of metals will set free sufficient heat to exert a noticeable influence on the speed of cooling, which may easily be detected if the temperature changes are observed with aid of accurate measuring instruments. In observing the slow cooling of a large reverberatory furnace filled with white bearing metals and plotting the find-

ings on a time-temperature curve sheet, the temperature curve will show a number of breaks corresponding to the temperature and extent of the solidification of the individual groups of crystals.

Methods of Production.—The first and simplest method of production is the ordinary liquation process at rising temperatures. The bars and slabs of white metal are placed upon the upper part of the

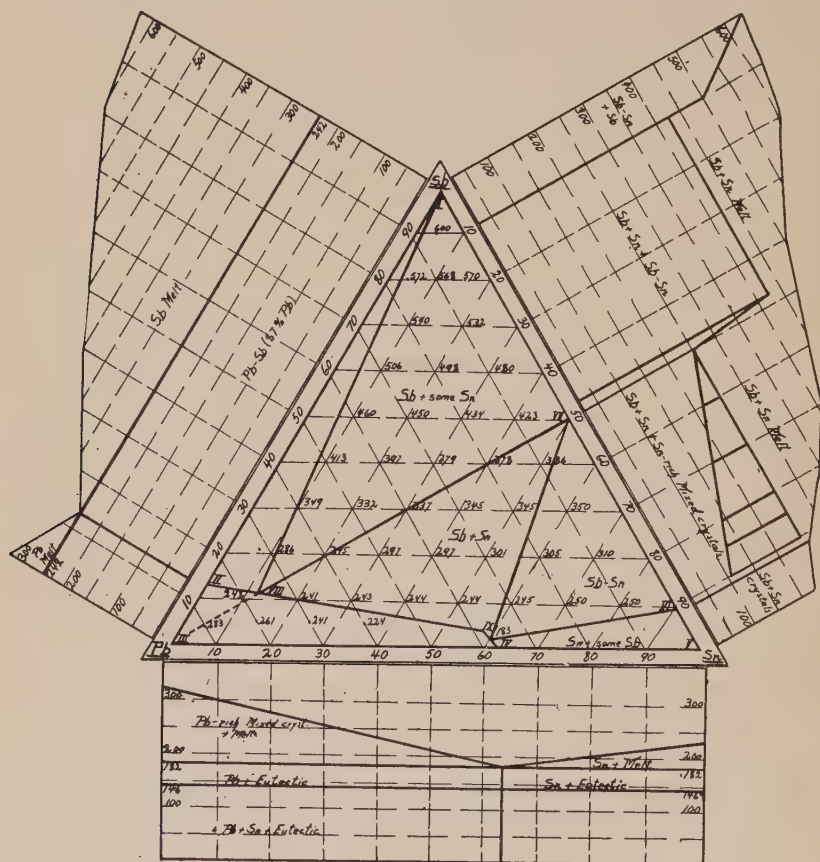


FIG. 16.—TERNARY DIAGRAM: LEAD-TIN-ANTIMONY.

flat inclined hearth of a reverberatory furnace and the eutectic alloy is liquated by maintaining a uniform temperature of about 183° to 185° C. The temperature is then slowly increased to about 190° C. and, after most of the alloying constituents melting at that temperature have been liquated off, to 195° C.; finally the temperature is

raised to 210° C. The liquated metal is permitted to leave the furnace, the products of each temperature interval being collected separately in order to assure of a perfectly separated and uniform product. This liquation process may be carried out in most all small and medium reverberatory furnace types, although cast iron liquation plans also have been used successfully for this purpose.

The main disadvantages of this method are the discontinuity of the process, the smallness of each charge, the length of time required for each run, the relatively high consumption of fuel, and the necessity of employing one man specially to attend to the firing and to operate the furnace. Nevertheless, this process is frequently used by small producers desiring to manufacture small quantities of tin-alloy to be used in the production of solder in their own plant.

Much better results may be obtained by modifying this primitive method, that is to say, by adding a relatively large melting pot to the furnace. Liquation of the alloy, instead of taking place at the melting temperature of the eutectic alloy, is then carried out at a temperature of about 187° C., thus obtaining a much more rapid liquation and separation of the fusible constituents of the alloy which flows into the melting pot, where it is finish-treated by applying the process of fractional crystallization.

The Modern Reverberatory Process.—It is clear from the discussion of the theoretical principles of the tin-alloy process that if a charge of white metal alloy is cooled down gradually until the metallic bath has reached a temperature of, say, 184° C., the entire charge will have separated into a solidified layer comparatively rich in copper and antimony, and the liquid eutectic alloy, which contains about 55 per cent tin, 3.5 to 3.8 per cent antimony, and 0.1 to 0.2 per cent copper, lead making up the rest of the composition. The logical development of this principle in connection with the logical construction of the reverberatory furnace employed has led to the development of the modern tin-alloy process.

In accordance with the principles underlying the process, the hearth of the furnace is made considerably deeper than is usual with reverberatory furnaces. (Figs. 17 and 18.) A pyrometer is introduced through the roof, the lower point of the pyrometer tube reaching to within about 1 to 2 in. of the hearth. In order to avoid excessive corrosion of the pyrometer tube by the hot metal, it is inserted into a seamless rolled iron tube, the lower end of which is closed by welding while the upper end is mushroomed, thus forming a support

for the tube and pyrometer. In order to prevent the entrance of air between tube and pyrometer, which would have an unfavorable influence on the pyrometer readings, the open space is filled with sand. Shutting up the hollow space by stuffing rags into the open end does

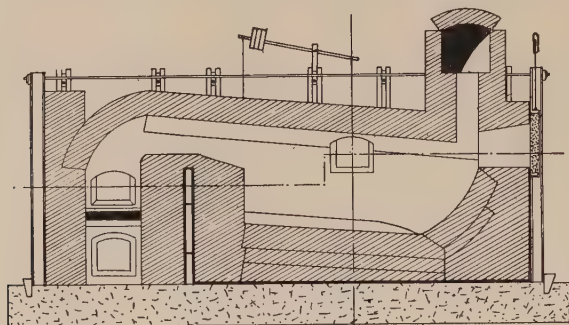


FIG. 17.

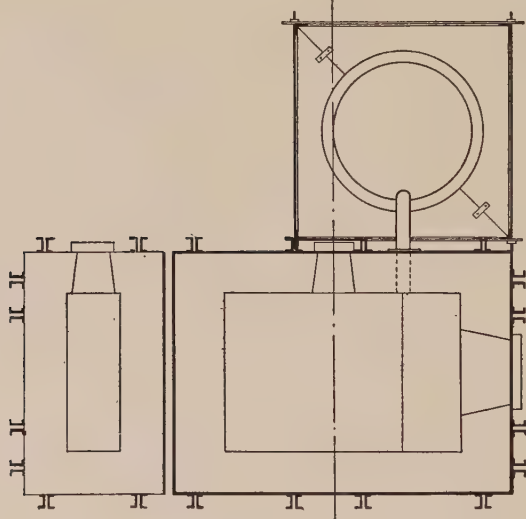


FIG. 18.

FIGS. 17 AND 18.—TIN-ALLOY FURNACE.

not produce the desired results, since the furnace atmosphere above the metal surface will cool off the corresponding layer of air inside the iron tube, which, in descending within the tube, will modify the temperatures at the critical part of the pyrometer.

Figures 17 and 18 show a section through a typical coal fired tin-alloy reverberatory furnace.

After filling the furnace, the surface of the metal is skimmed, the fire extinguished, and the metal left to cool down slowly. The pyrometer is not introduced until the temperature of the metal has dropped to about 475 to 550° Fahr., that is to say, until a crust begins to form. From this time on the further decrease of temperatures is closely followed and the measurements entered upon a curve sheet, thus providing for a sharp control of the progress and the end of the cooling process. A temperature curve is made of every charge, the decrease of temperatures being plotted at intervals of 30 minutes each, beginning at a temperature of 250° C., or 500° Fahr.

The cooling process is ended as soon as at a temperature of approximately 184° C. (363° Fahr.) the cooling curve proceeds horizontally for about 45 to 60 minutes, indicating commencing crystallization of the eutectic alloy, when the amount of heat generated by the crystallization of this material neutralizes the cooling effect of the outside temperature. The furnace is then opened and the liquid metal tapped.

After ladling out the first quality tin-alloy tapped, the furnace temperature and that of the metal is increased degree by degree, the second tapping taking place at a temperature about 5° C. (9° Fahr.) higher than the first, when a second quality tin-alloy is obtained which frequently suffices for use as tin-alloy. The analysis of this alloy averages about 53 to 54 per cent tin, 4.0 to 4.2 per cent antimony, and 0.2 per cent copper. A third and fourth tapping follows, containing increasing percentages of antimony and copper and correspondingly less tin until, finally, a material remains in the furnace which, by increasing the furnace temperature to dark redness yields sufficiently high copper and antimony contents to be suitable as primary alloy for the production of "Glanz metal." This material resembles the so-called "white matte" and may be finish-treated the same way.

Where the tin-alloy is being used for home purposes, that is to say, where the producer employs the alloy for the manufacture of solders or similar white metal alloys, the first and second tappings are usually mixed, while the third and fourth tappings are often added to the next charge, unless their composition qualify them for direct use in certain alloys in the process of manufacture. Later products of the

tin-alloy process are returned to the preliminary refining process for the partial elimination of their copper contents.

The chief disadvantages of this tin-alloy process¹ are:

1. The necessity of continual and sharp control of the temperature changes, particularly towards the end of the cooling process.
2. The fact that part of the eutectic alloy is not contained in the first tapped tin-alloy, since the only indication of the correct tapping temperature, the horizontal course of the temperature curve, is based upon the heat liberated by the commencing crystallization of the eutectic alloy.
3. The rather difficult tapping operation, which is due to the fact that a heavy layer of hard, solid material has formed over the inside of the tap. The loss of time thus incurred—about 10 to 15 minutes—causes additional loss of tin-alloy by crystallization.

These disadvantages can be eliminated by providing the furnace with a sufficiently large fore-kettle and tapping at a metal temperature of about 187° C. (368° Fahr.), continuing the process in the melting pots as described on page 137.

¹ German Patent granted to Hüttenwerke Tempelhof A. Meyer, Berlin, Germany.

CHAPTER X

THE SMELTING TREATMENT OF LEAD RESIDUES

Commercial lead residues may roughly be divided into six groups:

1. Lead drosses consisting of metallic lead and lead oxide in varying proportions,
2. Lead ashes from metallurgical processes,
3. Lead slags,
4. Dry lead oxides produced by the chemical industries, such as accumulator material,
5. Flue dust, dry or wet,
6. Dry or wet lead compounds, such as lead nitrate, etc., produced by the chemical industries.

Practically all of these residues, excepting, perhaps, those drawn from the various chemical industries, are more or less contaminated with other metallic constituents, mainly tin, antimony, zinc, and copper, necessitating modifications in their treatment, but this chapter will be confined merely to all the products of the chemical, metallurgical, and metal-working industries, containing comparatively small quantities of these impurities only.

The conversion of lead residues into refined lead by metallurgical processes takes place in two steps: (1) A preliminary smelting treatment in reverberatory or blast furnaces—or both—leading to the production of work lead, and (2) a refining treatment of the work lead in reverberatory refining furnaces, or, eventually, melting pot plants.

Opinions concerning the relative merits of reverberatory or blast furnace treatments, singly or in conjunction with each other, have always been sharply divided. While in European countries the blast furnace treatment of all lead residues containing less than 60 to 75 per cent lead, and a combined reverberatory-blast furnace treatment for richer lead materials, is considered the only efficient and economical solution of the problem, American and Canadian metallurgists

prefer the use of reverberatory furnaces for the treatment of most residues, irrespective of lead contents.

There can be no doubt that the reverberatory furnace represents the only logical melting device in comparatively small residue smelters, or wherever the amount of residues treated is not sufficiently large to assure of a continuous supply of certain minimum quantities. Blast furnace operation is efficient only with a daily average output of at least 10 to 15 tons. Frequent shut-downs of blast furnaces cause excessive loss of heat and waste of fuel, since each starting-up operation requires the use of several tons of coke and wood to heat up the furnace to its minimum working temperature.

Again, while some of the residues above named may be treated in the reverberatory furnace, most of them can be successfully smelted in the blast furnace only. It will be shown, however, that even with such materials as will, with careful treatment, give satisfactory results in reverberatory furnaces, the blast furnace will prove to be a most desirable adjunct.

In short, while the reverberatory furnace represents a highly important metallurgical unit for the preliminary treatment of residues, it may well be dispensed with or, eventually, superseded by other mechanical apparatus, such as briquetting presses. The blast furnace, on the other hand, is indispensable for any plant smelting large quantities of lead residues of differing origin and composition on an economical basis.

The Reverberatory Furnace.—The reverberatory furnace is particularly suited to the preliminary smelting of powdered oxide material which cannot possibly be charged into the blast furnace in appreciable quantities without first being slagged and briquetted. Its main disadvantage is the fact that even with most efficient smelting, not all the metal contained in the ashes can be economically removed from the raw material, the slags produced containing entirely too much metal to be discarded, but not enough to be retreated in the blast furnace with any chance of success. Quite frequently, the slags produced contain from 5 to 10 per cent of metal and metallic compounds, while ashes below a certain percentage of lead, say about 40 to 50 per cent, cannot economically be treated at all—unless reverberatory smelting represents an introductory process to the final blast furnace treatment.

In reverberatory smelting, the extraction of metal from the ashes or other lead residues should not, therefore, be carried too far. If

no blast furnace is available, and the reverberatory slags produced have to be sold to another smelter, the material will not find a favorable market at reasonable prices if too low in metal, while slags with 40 per cent of lead and more may easily be sold at correspondingly high prices. The lead produced with intensive extraction, on the other hand, contains most of the metallic impurities present in the residues, while the judicious extraction of only part of the lead will yield a comparatively pure product. In a mixture of the oxides of lead, copper, antimony, tin, iron, and zinc, carbon reduces the lead first, copper second, and iron last, so that it is evident that with careful operation a comparatively pure lead product is obtained. (The zinc oxide present cannot be reduced in the reverberatory furnace, of course.)

Thus, the chief advantages of the blast furnace treatment of lead ashes, as compared with the reverberatory furnace processes, are:

1. Saving of fuel,
2. Continuity of operations,
3. Larger capacity,
4. Better smelting conditions, particularly with material low in lead.

The main disadvantages of blast furnace smelting are:

1. Impossibility of charging powdery, small-grained material without previous briquetting or slagging.
2. Higher loss of metal by vaporization and dusting.
3. Continuous danger of trouble where many small lots of residues of different composition are being smelted.

The reverberatory furnace, on the other hand, works best with powdery material, its operation does not require continuous care and attention, so that throughout the smelting period one man can easily tend two furnaces. Indeed, there is no chance of "killing" the reverberatory furnace by wrong charge compositions or occasional lack of attention. On account of the lower velocity of the flue gases it permits of more perfect settling of metallic particles carried along mechanically, and of better condensation of metallic fumes in the flue channels. There are very much less fumes to contend with, a matter of great importance to smelters situated within or near cities and towns where sanitary police regulations in this respect are strictly enforced. The initial expenses of erecting a reverberatory

furnace plant are decidedly lower, since a blast furnace outfit requires the installation of blowers, cooling water tanks, etc. The same is true of operating expenses.

The various working methods employed in smelting of lead residues in reverberatory furnaces differ but little. As a rule, sand, lime, iron oxide and fluorspar are used as fluxes. Soda ash should not be used in smelting lead ashes. The use of this substance in the reverberatory smelting of white metal ashes, etc., has caused it to be considered somewhat of a panacea for all reverberatory smelting operations. However, apart from its purely physical property of melting to a thin liquid at the temperatures of the process, and thereby moistening the ashes, it cannot possibly influence them chemically, unless they are contaminated with silicious material. But there can be no doubt as to the strong action of soda ash on the furnace walls and bottom which, unless constructed of magnesite or chrome bricks, will be attacked and ruined within a comparatively short time.

The usual type of lead ashes may easily be liquated by mixing with coke fines, etc., and heating the mixture to sufficiently high temperatures (1600 to 1900° Fahr.). The soft mass formed will permit of perfect contact of the metal oxides with the coke particles, and of quite a good separation of the metallic lead produced. After removal from the furnace, the residues represent an ideal material for the final blast furnace treatment. The higher the furnace temperatures, the more complete will, of course, be the rate of extraction of lead. However, too high a temperature must be guarded against, in order to avoid too great a loss of lead and, eventually, tin by volatilization.

It is clear from the above that qualitatively best results are obtained in reverberatory treating of comparatively pure lead ashes by liquating or sweating rather than smelting.

This process of partial purification may be still further developed if, apart from limiting the amount of reducing carbon to about 2 to 3 per cent, the temperatures are reduced to about 1500° Fahr., and the furnace atmosphere maintained in as weakly a reducing condition as possible. For instance, if the lead-antimony oxide mixtures obtained during the last part of the lead refining process are mixed with about 3 to 5 per cent of carbon and treated in a coke fired reverberatory furnace with widely open air ports, the furnace atmosphere being clearly oxidizing, the antimony contents of the ashes

are concentrated in the furnace residues, while the metallic lead produced is almost pure. The slaggy or drossy residues obtained are then subjected to a final treatment in the blast furnace.

In general lead smelter practice all residues containing more than 60 or 70 per cent of lead should therefore be subjected to a preliminary reverberatory process, 50 per cent of the metallic contents being removed in a comparatively pure state, while the residues—now in the proper physical condition for blast furnace smelting—are completely extracted in the final blast furnace treatment. Since, as is generally known, powdery residues are not conducive to efficient blast furnace operation, care must be exercised to conduct the reverberatory process so as to obtain as slaggy and coarse a residue as possible. The addition of too much lime, for instance, may cause the formation of a dry and powdery material, which must then be converted into a slaggy condition either by adding silicious materials and heating to high temperatures, or by adding judicious amounts of soda ash. It should be pointed out, however, that the presence of considerable percentages of soda ash in blast furnace mixtures causes the production of undesirable slags, so that an excess of lime in reverberatory furnace charges should either be avoided in the first place, or the strongly powdered condition of the products be remedied by adding silicious materials.

While a great deal of attention is usually paid to the composition of the charge mixtures, the general tendency being to complicate matters as much as possible, too little weight is often put upon the correct treatment of the charges during the smelting process. Contrary to the blast furnace, reverberatories will smelt most anything if the temperatures, composition and nature of the gases of combustion, and the mechanical treatment of the charges correspond with the nature of the material in question. The following rules should be observed when treating the ordinary type of lead ashes:

Before charging, the furnace should be sufficiently preheated. A temperature of about 1600° Fahr., maintained for three or four hours, suffices for this purpose.

Dry materials, especially if present in a powdery condition, should be moistened before charging in order to prevent excessive dusting during charging and throughout the first period of the process.

Immediately before charging, a few shovelful of powdered coke are spread over the hearth. The residues are then charged. The amount of coke fines added with the residues depends on the lead

oxide contents as well as on the amount of tin and antimony present. As a rule, one shovel of coke fines is allowed for five shovels of lead ashes.

The total amount of residues charged depends in the first place upon the hearth area. With average material, the layer should be about 6 to 8 inches thick. Very rich residues may be given 2 or 3 inches more, provided there is no lack of rabbling.

Diligent rabbling tends more than intricate charge compositions to raise the efficiency of the process. The charge should be thoroughly worked over, and one or two shovelsful of powdered coke be spread over the charge, at least every half an hour.

About one or two hours after charging, lead commences to form copiously, while the bulk of the lead contents has separated out after three or four hours. Continuing the process much longer is not to be recommended, since the trouble and expenses incurred do not pay for the small amounts of metal obtained. It is possible, of course, to remove practically all of the lead contained in the residues by raising the furnace temperatures to above 2000° Fahr., but the loss of metal by vaporization and the excessive wear of the furnace linings are disadvantages which, in view of the small margin of profit possible, appear too serious to justify this method of treatment.

The more or less pasty slags often obtained contain an appreciable amount of metallic lead in form of small globules, which cannot be removed by any amount of rabbling. Raising the temperatures, which, if carried far enough, would effect the settling of the metallic lead, is not to be recommended for reasons already explained, but a large proportion of this metal may be made to separate out by adding a few shovels of lime, mixing thoroughly, and waiting about half an hour before removing the residues from the furnace. Attention is again called to the fact that an excess of lime will render the material too dry for blast furnace smelting. Metallic iron in form of thin-walled scraps may also be employed for this purpose.

Blast Furnace Smelting.—The chief advantages of the blast furnace treatment of lead residues are as follows:

1. Continuity of process and a correspondingly greater capacity per unit and per capital invested.
2. A considerably better separation of the various constituents of the materials, or of the impurities contained.
3. Better and poorer slags.
4. Lower fuel consumption.

In order to understand fully the principles underlying the blast furnace process, the reactions taking place between the different constituents of the lead bearing materials, the slag forming substances, and the coke must be understood.

Lead blast furnace charges consist of the different lead residues, iron and iron oxides, lime, coke, and "returned slag." The impurities present in metallurgical lead residues are for the most part: antimony, tin, zinc, and copper, while the residues obtained from chemical works contain hydrochloric acid, sulphuric acid, zinc chloride, etc.

The metallurgical residues, slags, ashes, dross, etc., should form the main part of the charges, while the chemical products and the flue dust should be added in small quantities only. Particular care should be exerted in adding accumulator material, since the sulphuric acid contained in the mud may lead to much trouble. If, on account of lack of other suitable residues, accumulator mud has to be added in considerable quantities, correspondingly large amounts of lime and returned slag should also be added in order to neutralize the deleterious effects of the acid.

The disadvantages connected with the use of materials containing hydrochloric acid and volatile chlorides are mainly due to the formation of metallic chlorides, which increases the loss of metals by volatilization, and decreases the value of the flue dust contaminated with these chlorides, since large deductions in price are usually effected for metallic residues containing chlorides. The only way to prevent, or at least minimize, this trouble is to give the residues concerned a preliminary treatment in the reverberatory furnace, adding correspondingly large amounts of sodium carbonate to the charge which absorb the hydrochloric acid and neutralize the material. The temperature of the reverberatory furnace should not exceed 1250° Fahr. to avoid fuming of the chlorides. The residues obtained by the reverberatory treatment are then crushed and washed, so as to remove the sodium chloride formed and are then either re-treated in the reverberatory, or briquetted and charged directly into the blast furnace. It is self-evident, of course, that small quantities of this dechloridized material need not be specially briquetted for treatment in the blast furnace if the chief constituents, or the bulk, of the blast furnace charges are sufficiently coarse. One or two shovelful of this material spread over the rest of the charge will not materially disturb the free passage of the blast through the charge column, although the loss of metal by dusting is slightly greater than with briquetted or slagged material.

CHAPTER XI

LEAD SLAGS

Since it is the object of blast furnace smelting to separate the lead and other valuable metallic constituents of the charges from the non-metallic constituents, fusible slags must be produced, the nature and composition of which are of decided influence on the success of the process. Where the slag forming materials are not contained in the residues, silica and the various basic constituents of the slag must be added in the requisite quantities.

Apart from the chief purpose of slags above indicated, they are also useful in protecting the metallic lead produced against the strongly oxidizing influence of the blast. In addition, the observation of the physical and chemical properties of the slags produced, their composition, color, degrees of viscosity, manner of freezing, etc., will indicate the progress of smelting operations, the state of the furnace, and the eventual sources of trouble. Thus, while it is perfectly visible in many instances, to smelt certain residues merely by the addition of sufficient coke, satisfactory results can never be obtained if the blast furnace process is carried out without the presence of slag forming elements.

“Good” slags must exhibit the following general properties:

1. Slags must be thoroughly fusible and flow easily at ordinary furnace temperatures.
2. They should not be viscous and possess a low specific weight, so as to minimize their resistance against the passage of the descending metals and metallic compounds (Speise, Matte, etc.).
3. They should be chemically neutral towards the metals and compounds passing through them, as well as towards the construction materials of the blast furnace.
4. The above properties must be attained at minimum costs.

Influence of the Components on the Properties of Slag.—Since efficient blast furnace operation is only possible if the variations of compositions and general physical properties of the residues to be

treated are carefully considered in choosing the type and composition of the slags, the influence of the various desirable and undesirable constituents of the slags on their chemical and physical properties must be understood. The slag forming materials usually required are iron, limestone, sand and, occasionally, fluorspar. Manganese also is sometimes used, while the limestone is usually contaminated with considerable quantities of magnesia, the properties of which must also be considered.

Iron Oxide.—The larger the percentages of iron contained in the slag the higher the degree of fusibility and liquidity and the specific gravity of the slag-compositions. Slags containing excessive amounts of iron are distinctly disadvantageous for the following reasons:

1. The specific weights of the slags are too high, increasing the resistance against clean separation of matte and speise.

2. Iron sows are easily formed, since part of the excess iron oxide added is reduced to metallic iron instead of entering the slag. Reduction of a certain quantity of ferrous oxide to the metal is absolutely necessary, of course, to assure of perfect reduction of the lead sulphide present, which is only effected by metallic iron, but the iron reduced in excess of the amount necessary for this reaction must be reoxidized or sulphurized to enter the slag or the matte.

3. The construction material of the furnace, including the refractory lining and the iron material (spouts, etc.), is rapidly corroded.

4. The melting temperatures of these slags are too low to permit of the quantitative reduction of ferrous oxide to metallic iron necessary to effect perfect decomposition of lead sulphide materials.

The ordinarily used percentages of iron oxide in lead slags (38 to 43 per cent) should only be exceeded where high zinc contents of the raw materials are desired to be slagged. High ferrous oxide contents do not only increase the absorptive and solution capacity of lead slags for zinc oxide, but assist greatly in the oxidation of zinc sulphide, thus avoiding the formation of zinc sulphide accretions at the upper part of the blast furnace shaft.

Lack of ferrous oxide in lead slags causes them to become viscous. The fluxing capacity of the iron material used is directly proportional to its degree of purity, since only that part of the iron or the iron oxides becomes available which is not taken up by the silica, sulphur or arsenic contents of the iron ore used.

Manganese.—The influence of manganous oxide in lead slags generally resembles that of ferrous oxide, and this may therefore be

substituted for the latter if necessary. However, since this compound tends strongly to increase the fusibility and liquidity of slags, large amounts of manganous oxide require the presence of correspondingly larger percentages of silica.

Another characteristic property of manganous oxide, distinguishing it from ferrous oxide, is its comparatively high oxidizing power, which tends to decrease the amount of matte and speise formed, increasing at the same time the loss of copper by slagging. It does not, however, appear to exert a noticeable influence on the slagging of lead. The claim frequently made that lead slags rich in manganese tend to absorb excessive quantities of silver has not been substantiated in many other instances, and it appears that the large silver contents found in high manganese slags are chiefly due to other factors which escaped the attention of investigators.

The characteristic peculiarities of manganese contents in lead slags do not, as a rule, become noticeable unless the amount of manganese dioxide in the charge exceeds 10 to 12 per cent,¹ a quantity hardly ever found in charge compositions used in residue lead smelters.

Lime.—The most important characteristics of lime contents in lead slags are the decrease of the specific weights and viscosities, facilitating the settling of matte and speise, and preventing excessive absorption of these products by the slag. Due to the higher melting point of suitable lime slags, they require more fuel, a stronger blast and a higher charge column, that is to say, a higher furnace, than slags poor in lime and richer in iron.

Of particular interest is the influence of lime on the slagging of zinc oxide. The higher the percentage of lime the less zinc oxide is taken up by the slags and the larger the amounts of zinc oxide volatilized. With a lime content of 28 per cent and more the slag has completely lost its absorption power for zinc oxide, all the oxide produced being volatilized, contaminating the flue dust and forming incrustations at the upper parts of the furnace shaft. While with proper construction of flue dust catching devices this separation of most of the zinc contents of lead residues in the form of impure zinc oxide may appear to be perfectly desirable, and while a number of large European residue smelters are actually separating the zinc contents of their residues by this process, it should be considered that with high zinc charges the difficulties encountered in blast furnace

¹ Furman, *School of Mines Quarterly*, XIV, p. 315.

operations are noticeably accentuated by comparatively small increases of the lime contents of slags above the maximum of about 16 per cent.

Since, on the other hand, limestone or other lime materials are always cheaper than iron fluxes, the tendency of practically all lead smelters is to produce slags rich in lime, the use of this fluxing medium being limited only by the character and the amount of foreign matters contained in the residues. The cheapest and most available lime flux is lime stone. Since it is practically impossible to obtain cheap and high grade limestone in all localities, the more common varieties containing more or less magnesia are usually employed for this purpose. Smelting works located near the coast often take advantage of the large supply of oyster shells available during certain seasons of the year, which are highly adapted for use as lime flux, being practically free from magnesia.

Magnesia.—Although the influence of small percentages of magnesia in lead slags is similar to that of lime, larger quantities of this material are absolutely undesirable in lead blast furnaces, especially if considerable percentages of zinc are present at the same time. Zinc oxide and magnesia in larger quantities tend to form the ill-famed Spinell. The limits of analogy with lime are determined by the considerably higher melting temperatures of the magnesium silicates.

Fluorspar.—Fluorspar possesses a melting point of 1300° C. and a high degree of fluidity. It forms readily fusible compounds with the sulphates of calcium and barium, and assists in fluxing the sulphide and oxide of zinc, which form important constituents of the accretions often found at the lower sections of blast furnace shafts. For these reasons, fluorspar is often used where charges of a difficult nature have to be smelted, one or two shovelful of this flux being spread out over each charge, or wherever the descent of the charge column is not as rapid as at other points.

CHAPTER XII

THE CONSTRUCTION AND OPERATION OF LEAD BLAST FURNACES

In view of the special character of the present volume, the construction and operation of only those lead blast furnaces will here be considered which are best suited to the treatment of residues of lead and lead alloys. No attention will therefore be paid to the large rectangular blast furnace constructions used in ore smelters, while only passing mention will be made of the more ancient types of lead blast furnaces, which may be regarded as forerunners of the present large lead ore blast furnaces. There can be no doubt, however, that a large number of small lead residue blast furnaces constructed by small sized residue smelters in America and, particularly, Europe, possess most of the characteristics of these old inefficient constructions untouched by any of the modern improvements. The author has seen a number of "blast furnaces" made from old boiler shells which, according to the smelter officials, worked "surprisingly well," without, however, enabling them to smelt any of the ordinary residues at a loss of less than 15 per cent.

It is obvious that in view of the comparatively small and irregular supply of lead residues, and the peculiar nature of many of these materials, the small round or rectangular blast furnaces will render most efficient service. Of these, the latter type is best suited to home construction.

While these small blast furnaces may be operated with internal crucibles, of course, much better results are obtained if the internal crucible is omitted and the furnace is supplied with a forehearth, all the products of the process, lead, matte, speise, and slag, being run into the forehearth where they are separated by specific gravity. Since smooth operation of such a forehearth, subjected as it is to the cooling influence of the outside air, requires a certain amount of heat reserves in the smelting products collecting in the forehearth, it is unsuitable to blast furnaces of very small capacities, the per-

missible minimum being about 15 tons of lead per day. Smaller lead blast furnaces should be operated with internal crucible.

Another decided improvement may be effected by mounting the hearth section of the furnaces on wheels, rendering it removable or exchangeable for the purpose of cleaning or repairing. These movable hearths are applicable to furnaces operating with or without internal crucibles.

One of the chief advantages of the removable blast furnace hearths is the perfect degree of accessibility of the interior of the furnace for the purpose of cleaning and repairing hearth and shaft. While furnaces with fixed hearths are kept in operation for months at a time until the increasing thickness of accretions or other internal troubles make continuation impossible, furnaces with removable hearths may be stopped any Saturday afternoon, cleaned and repaired by a special crew throughout Sunday and "blown-in" on Monday morning, thus being in full operation not later than Monday afternoon. In this way the furnace is at all times kept free of heavy accretions, serious difficulties are soon discovered and overcome, and the efficiency of the unit is constantly maintained at a uniformly high degree. Figures 19 and 20 illustrate the type of furnaces described, which has been in constant operation at European smelters for a number of years.

Figure 21 shows a small blast furnace constructed by the Colorado Iron-Works Company, which is admirably adapted to the recovery of lead from various waste metals.

The furnace is used in two sizes, 20-inch and 26-inch internal diameter at the tuyère level. The water jacket is of steel plate, divided vertically in halves, and extends upward to near the charging floor level. The jacket, together with the charging hood and stack, is carried by a steel frame supported by four columns. The crucible is mounted on a truck and in operation is raised up close to the lower edge of the jacket and slightly above the rail track by four jack screws. This feature, together with the vertical division of the jacket makes cleaning out in the event of a freeze-up as simple and rapid as is possible. The rectangular drum at the extreme top in the illustration is the drum of a Nesmith jacket water vaporizer. This device is claimed to maintain the jacket water at an even temperature, thus promoting even running of the furnace, and reduces the quantity of cooling water to one-eighth that required without it.

Figure 22 represents a large capacity blast furnace for the smelting of lead materials also built by the Colorado Iron Works Company.

Figure 23 shows a modern design of the lower part of a 36-inch $\times$ 108-inch silver lead blast furnace with flange steel water jackets and arched bar mantles. The tuyères are of cast-iron with removable cap, whereby the entire area of the tuyères is obtained for removing slag, barring, etc. The blow pipes are made of gas pipe, in each of which is provided a quick opening gate valve, by which means each tuyère is under absolute control.

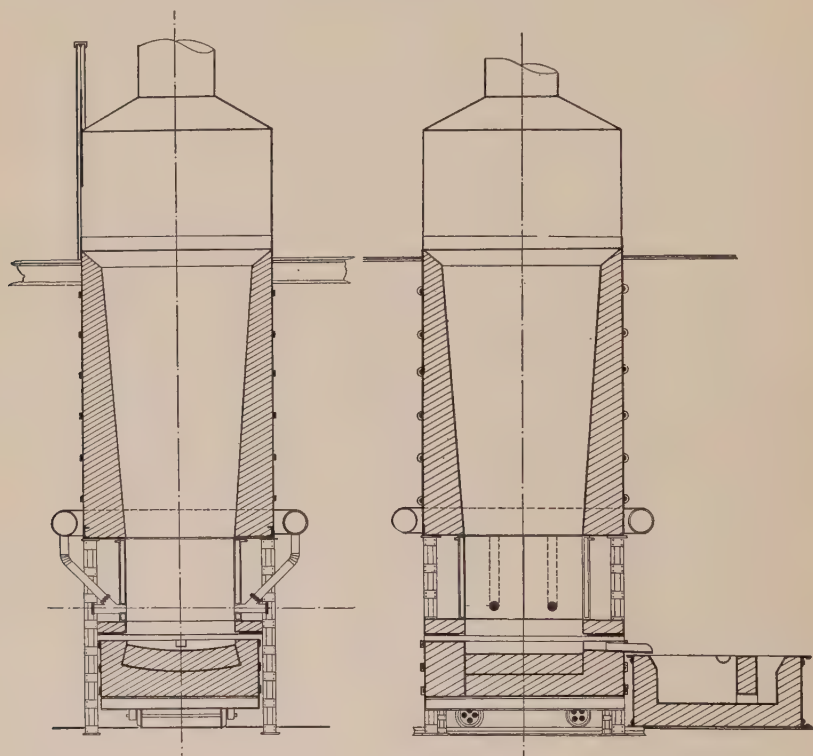


FIG. 19.

FIG. 20.

FIGS. 19 AND 20.—LEAD BLAST FURNACE.

Every modern lead blast furnace supplied with internal crucible as well as every forehearth should be provided with an Ahrent's automatic tap wherever the daily capacity exceeds 12 to 15 tons of lead. This limitation is especially important in the case of forehearths, since their successful operation is entirely dependent on the maintenance of sufficient heat to keep all the products in a thoroughly

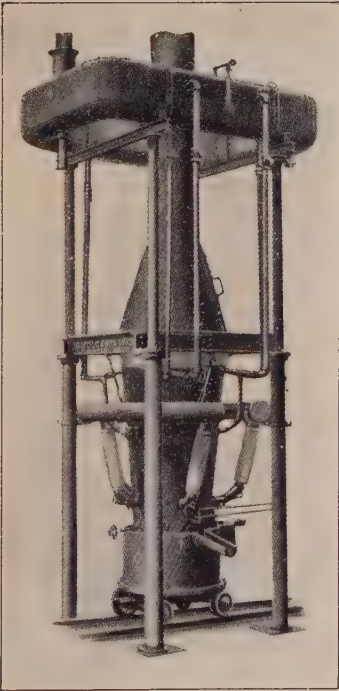


FIG. 21.—SMALL LEAD BLAST FURNACE.

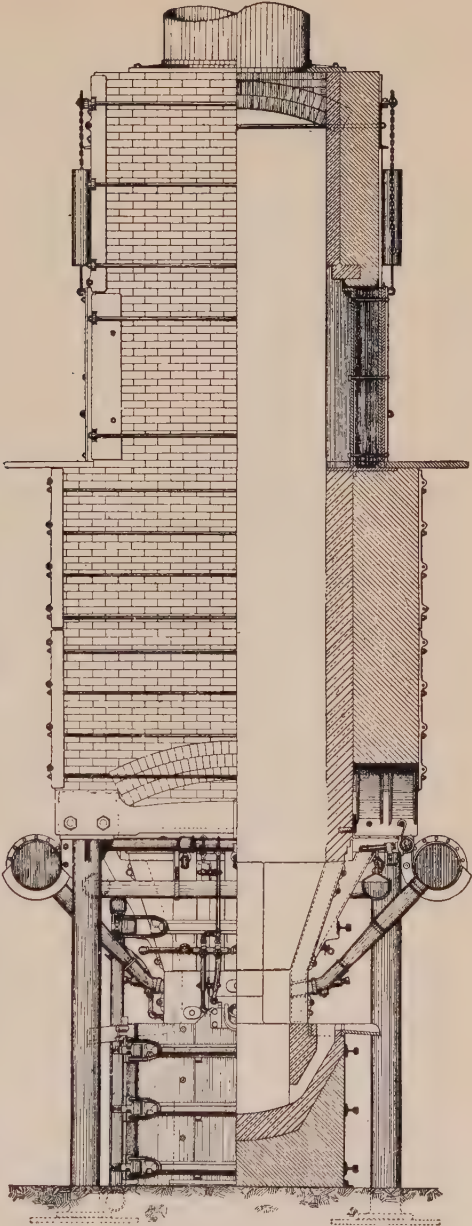


FIG. 22.—LARGE CAPACITY LEAD BLAST FURNACE.

liquid condition which can only be supplied by a uniformly heavy stream of white hot metal and slag from the furnace.

Cooling Jackets.—The most important section of the lead blast furnace is formed by the cooling jackets with the tuyères, which are placed on the walls of the hearth. The height of the individual jackets ranges from 3 to 4 feet, the width from 2 to 4 feet, and the thickness from 4 to 6 inches. The figures given represent the customary minimum and maximum dimensions. If the height of the cooling jackets be decreased to less than 3 feet, the brick walls immediately above will be attacked by the enormous heat and the strong chemical action of the melting zone, while a height of more than 4 or, perhaps 5 feet, must be considered excessive for even large lead

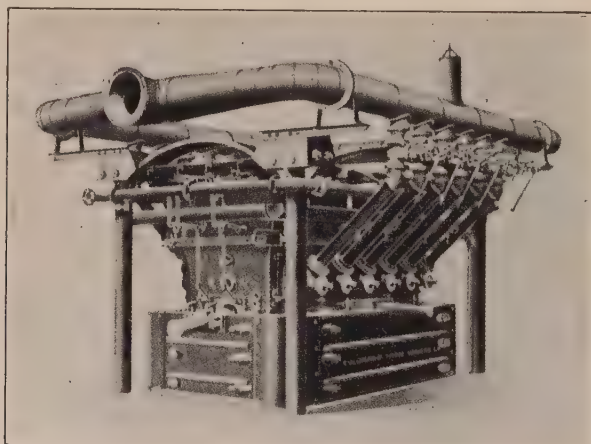


FIG. 23.—SILVER LEAD BLAST FURNACE.

blast furnaces, being much better adapted to the much more severe conditions obtaining in copper blast furnaces, and resulting in unnecessary loss of heat.

This heat saving principle has, however, been strongly attacked by a number of authorities, who claim that hot gases will carry along considerably larger amounts of flue dust and metallic vapors than cold gases, and that in spite of the heat transferred to the descending charges the heat of the ascending gases remains high enough to carry excessive quantities of metallic values out of the furnace. As a result, the cooling jackets of a number of American lead blast furnaces operated by lead ore smelters have been raised almost to the level of

the charging floor. While originally two rows of cooling jackets were provided, the size of individual jackets has gradually been increased to 8 to 10 feet.

It will not be attempted here to argue the merits of this change of principle. Suffice it to say that while the extraordinary cooling effect of very high water jackets may not exert serious influence on the blast furnace process with capacities of several hundred tons a day, small furnaces such as used in residue smelters would never run satisfactorily unless the proportion of coke would be increased accordingly. Although it is possible, of course, for any good furnace crew to smelt lead ores and residues in almost any kind of blast furnace-like contrivance, none but the usual low type of cooling jacket will give perfectly satisfactory results, particularly if only residues are treated; the small margin of profits left even with most economical smelting methods does not allow of the addition of more than the usual amounts of coke (8 to 9 per cent) or of large quantities of expensive fluxes. To effect the condensation of metallic vapors by cooling down the temperature of the stock, which by the very principle of blast furnace smelting is to be efficiently preheated to the high temperatures of the melting zone, appears to be rather inconsistent. Similar results may well be achieved in a more economical and convenient manner by cooling the top of the stock by means of proper construction of the charging section.

The width of the individual jackets is not of deciding importance as long as it does not tend to render the jackets too unwieldy to enable a quick exchange of jackets during a smelting campaign.

Every jacket is supplied with a separate water supply, the cooling water entering the jackets at the upper left corner while the warm water leaves at the upper right corner of the jacket. Circulation of the water within the jackets is effected by the difference of specific weight of hot and cold water, the fresh, cold water descending at the left side of the jacket and, warming up rapidly, ascending at the right hand side. The installation of partitions within the jacket for the purpose of regulating the circulation of cooling water is absolutely unnecessary and tends to accentuate the bad effects of heating strains.

Tuyères.—The tuyères serve to supply the air and oxygen necessary for the smelting reactions. Figure 24 shows the shape and construction of one of the most efficient types of tuyères available.

The bottom of this type of tuyères is provided with a circular opening covered with a thin disc of some low melting sheet metal,

such as zinc. If slag should enter the tuyères, it will melt the sheet and drop down harmlessly instead of bursting the peep-hole windows and scattering all over the neighborhood of the blast furnace. The tuyères are connected with the air main surrounding the furnace either by bags made of canvas or duck impregnated with water glass or some other air tightening, non-combustible substance, or by rigid sheet iron pipes, the chief advantage of the latter being their incombustibility. While in the case of air bags the flow of the blast may be regulated by means of string or wire tied around the bags, sheet iron pipes must, of course, be provided with gates.

Figure 25 illustrates one of the types of tuyères brought out by the Colorado Iron Works.

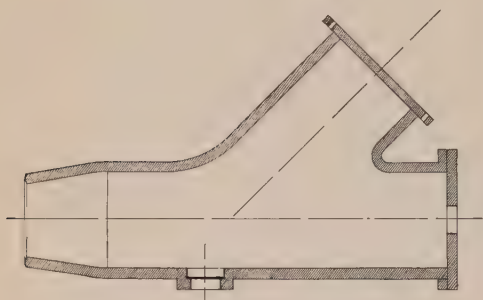


FIG. 24.

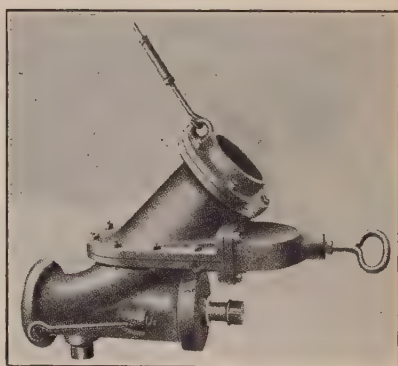


FIG. 25.

FIGS. 24 AND 25.—LEAD BLAST FURNACE TUYÈRE.

The diameter of the tuyères may range from 2 to 3 inches, depending upon the hearth area and the number of tuyères employed. A 2-inch tuyère may be considered sufficient for about $11\frac{1}{2}$ sq. ft. of hearth area, while a small blast furnace of a diameter of about 3 ft. should be supplied with 4 or 5 tuyères.

The shaft of residue lead blast furnaces rarely extends more than 8 to 10 feet above the cooling jackets. The thickness of walls just above the jackets amounts to about 18 inches, decreasing to 9 inches at the level of the charging floor. Excessive radiation of heat from the hottest part of the shaft is thus prevented, and sufficient contraction of the shaft provided to secure more perfect and rapid combustion.

Charging Devices.—The charging of stock and the removal of gases and vapor may be effected in one of three different ways as indicated in Figs. 26 to 29.

The most common charging device is that shown in Fig. 26, consisting of a sheet iron hood containing one or two charging doors. The hood may also be constructed of sheet steel or, preferably, brick-work, and leads directly up to the stack. The charging doors must be large enough to permit of efficient and comfortable charging as well as free and unobstructed handling of bars and chisels in removing accretions from the upper parts of the furnace walls or in general shaft cleaning work. The doors must therefore be at least 4 ft. high. Under no circumstances, however, should the lower edge of the charging doors be flush with the charging floor, and a sill at least 4 in. high should be provided to prevent the charging hands from just pushing the stock into the furnace, causing separation of the various constituents of the charge. A detailed description of charging operations is given on page 175.

Figures 27 and 28 illustrate the second type of charging device which is particularly suitable to the larger rectangular lead blast furnaces, but which may also be successfully applied to square or even circular blast furnaces if due attention is paid to correct charging methods. The gases and vapors are drawn off through a hood hanging about 10 to 20 inches into the throat of the shaft, and leaving enough space—about 25 inches—at the four sides for the descent of the charges into the shaft. Attention is called to the fact that the guard plates affixed to the upper edges of the shaft must be vertical in order to avoid clogging of the stock previous to entering the shaft proper.

The advantages inherent to this charging device are as follows:

1. The ascending furnace gases and vapors are drawn up through

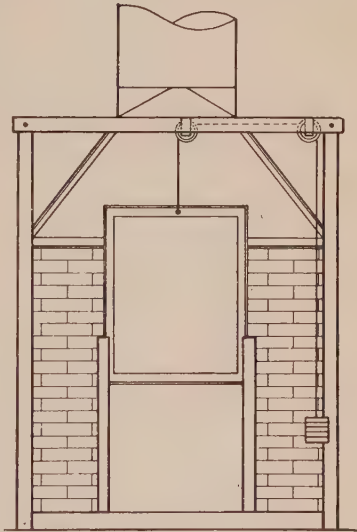


FIG. 26. — CHARGING DEVICE FOR LEAD BLAST FURNACE.

the center of the shaft instead of along the walls, giving up their heat and exerting their chemical influence where this is most needed.

2. By ascending through the center of the charge column the flue dust particles are much more effectively retained.

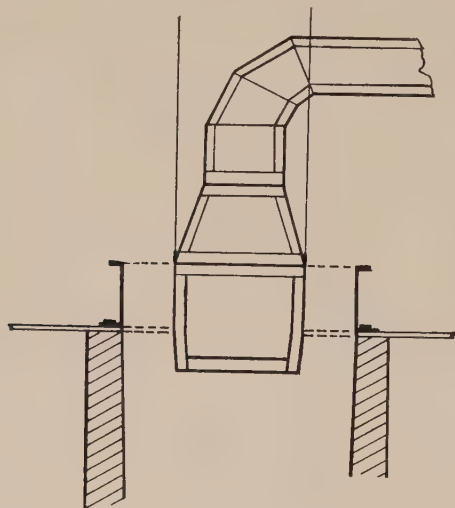


FIG. 27.

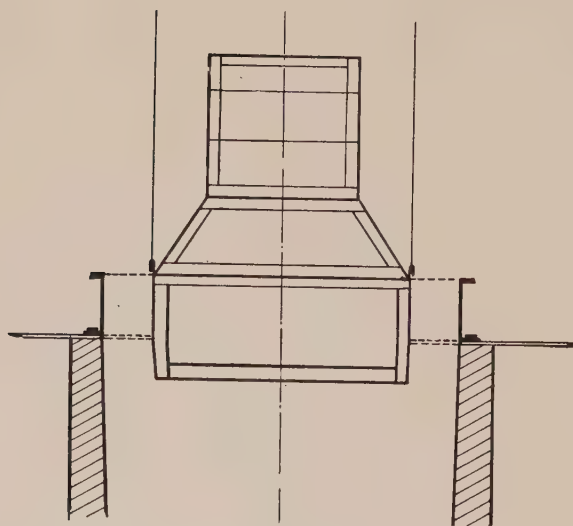


FIG. 28.

FIGS. 27 AND 28.—CHARGING DEVICE FOR LEAD BLAST FURNACE.

3. The cold air drawn in through the upper part of the charge from above does not merely effect the cooling of the top of the charge column, thus preventing the flaming of the furnace, but will also tend to condense comparatively large amounts of lead vapor otherwise carried into the flue dust chambers or into the air.

4. On account of the diversion of the metallic vapors from the cold walls of the shaft, the formation of accretions is practically prevented.

The reverse principle of charging is applied in the third charging device, Figure 29, where the charging hopper takes up the entire mouth of the shaft while the gases are drawn off at the sides.

This type of construction is particularly adapted to mechanical charging, since drop-bottom cars may be moved across the throat of the furnace to unload their charges into the hopper.

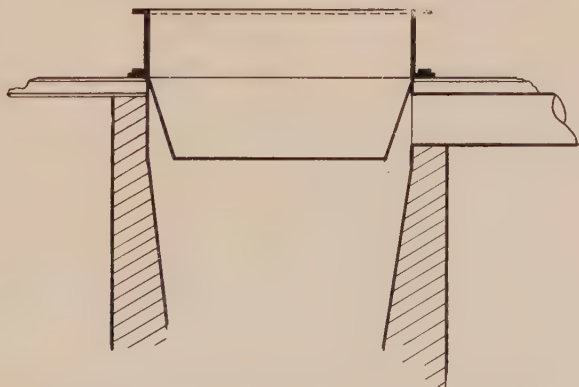


FIG. 29.—CHARGING DEVICE FOR LEAD BLAST FURNACE.

Forehearts.—The smaller types of lead blast furnaces should be constructed with internal crucibles unless the daily capacity exceeds 10 to 12 tons of lead. The chief advantage possessed by internal crucibles of small furnaces is the possibility of keeping lead and slag sufficiently hot for a considerable time, thus permitting a practically perfect separation of the slag from the other smelting products. The most important practical disadvantage, on the other hand, is the trouble invariably caused by the frequent opening of tap holes, and the fact that at each tapping of the lead and slag the surface of the slag and the part of the charge column immediately above it will be carried down quickly, passing the tuyères and the

smelting zone too rapidly to be smelted sufficiently, and thus contaminating the slag with considerable metal values.

These serious disadvantages are effectively avoided by eliminating the crucible and employing the various types of forehearth shown in Figures 30 to 32.

Forehearths may be constructed for continuous or intermittent operation. The intermittent type consists of a rectangular or round box made of cast iron plates and lined with fireclay bricks and fireclay mortar, which should be mounted on wheels or rollers to permit of easy removal or replacement. The box may be lined with fireclay or magnesite bricks, or with a clay or magnesite mass tamped down to form a spherical trough. (Fig. 30.)

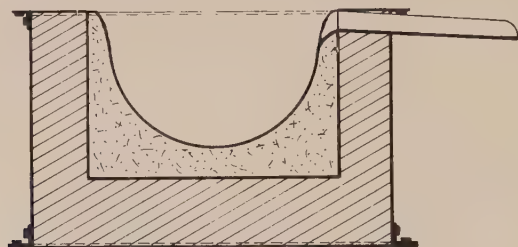


FIG. 30.—FOREHEARTH FOR LEAD BLAST FURNACE.

Lead and slag are permitted to flow into this forehearth together as fast as formed. The lead accumulates on the bottom of the trough and the slag runs over a spout into the slagpot. As soon as the forehearth is filled with lead, the furnace is closed, the lead ladled out quickly, and the process continued.

The advantages of this simple type of forehearth are as follows:

1. Its operation is exceedingly simple, and the most unskilled of attendants is perfectly able to operate it.
2. It may be used with rather small types of lead blast furnaces of comparatively low capacities, that is, down to about 12 tons a day, as against a minimum capacity of 15 to 20 tons in the case of the more modern types of forehearths supplied with syphon.
3. The forehearth may be completely relined and overhauled within a few hours.

The main disadvantages of this type of forehearth are its discontinuity, which precludes it from use with lead blast furnaces of larger capacity, and the unsatisfactory separation of the metallic lead from slag and matte as soon as the forehearth becomes filled with lead.

Continuity of process and a good separation may be effected by employing a forehearth illustrated in Figures 31 and 32.

Operation of Lead Blast Furnaces.—Blast furnaces, no matter how well constructed, will render satisfactory service only if due attention is paid to all the numerous details that make for efficient operation. The various chronic difficulties often experienced with lead blast furnaces, and which even old and experienced operators insist on blaming on inherent peculiarities of each individual furnace, are due not only to some error in construction, but more frequently to negligence concerning certain details usually considered of small practical importance.

Work on the Charging Floor.—The materials composing a charge are usually brought into position around the furnace by means of hand cars, although in some of the smaller plants wheelbarrows are

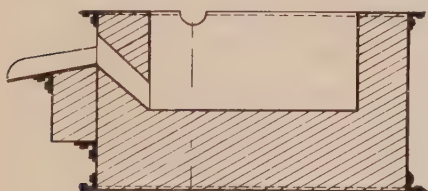


FIG. 31.

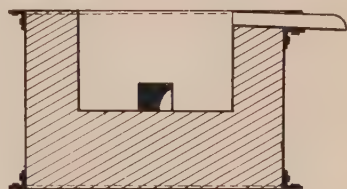


FIG. 32.

FIGS. 31 AND 32.—FOREHEARTH FOR LEAD BLAST FURNACE.

still being employed for this purpose. All material sent up to the charging floor must be accurately weighed in order to permit of perfect control of the flow of material. Coke should be charged into the cars by means of forks to prevent the fines from being charged into the furnace.

A great deal of attention should be paid to the correct placing of the individual layers of components making up a charge since, apart from determining the success of the melting process, efficient application of the principles underlying the relative position of the various charge materials permits of perfect control of the smelting reactions in a number of ways. Thus, under the ordinary charging conditions found in residue smelters, the fuel should form the lowest layer of a complete charge, followed by the metallic residues, the fluxes, and the slag in the order named. The order of the acid and basic flux layers depends upon the particular condition of the process. For instance, if it is found that the furnace temperatures are too

low for efficient operation, the nature of the flux following the layer of residues should coincide with that of the residues. With basic residues, iron oxide and lime should follow the layer of residues, while in the reverse case, that is to say, with strongly acid residues, siliceous slag material should be deposited next to the residue layer. Reversing this order of things will tend to lower the furnace temperatures, while still lower temperatures are induced if the residues and fluxes are mixed before charging, the coke forming the lowest layer, and with the slag on top of the charge.

With mechanical feeding, or where the charge column does not take up the whole of the shaft, necessitating dumping of the charge materials from a considerable height, the order of the various layers should be changed so as to place the coke on top of the charge. This is due to the fact that much of the coke would be crushed by the heavy material charged on top of it, decreasing the porosity of the coke layers and preventing sufficiently free ascent of the air, besides decreasing the reactive capacity of the fuel. The same order of charging should also be observed where the residues contain much finely powdered and difficultly reducible material which if the layer of residues would be deposited directly on the fuel, fills up the pores of the coke, decreasing its combustibility and causing it to reach the melting zone in a partly undecomposed state.

In presence of much fines, these are often charged separately, that is to say, the various coarse materials are charged in the usual order, while the fines are then fed here and there over the charge, trickling down through the coarse charge gradually but generally remaining with their own charge until this has reached the melting zone.

Of greatest importance to the success of blast furnace operation is the determination of the weight of the charges most suitable to the shaft area and to the nature of the materials smelted. It is known that efficient smelting depends upon the right weight of the charges, and that incorrect weights will invariably endanger the result obtained. One of the most common difficulties introduced by insufficiently large charges is the appearance of top fire, which in general furnace practice is usually due to excessively strong air blast, or to too large or too small percentages of fuel in the charges. This phenomenon may also be caused by incorrect construction of the furnace and by the formation of heavy accretions along the walls of the shaft.

The relation of the size of the charges to the formation of top fire is due to the fact that with insufficiently large charges the consecutive layers of fuel follow each other close enough to actually enable the heat, driven on by the air blast to climb up from coke layer to coke layer until it reaches the surface of the charge. (See also pages 25 and 26.)

Apart from the purely mechanical side of the work on the charging floor, it is necessary for the operator in charge to observe all irregularities connected with the appearance of the charge surface and the descent of the charge column which indicate the presence of disturbances in some part of the furnace. In view of the many different sources of disturbances, each of which may be brought about by a number of causes, it is obvious that irregularities of the charge surface alone will rarely point to the source of the troubles in question, observation of all the important parts of the lead blast furnace, such as the tap, the tuyères, temperature of the cooling jackets, etc., being required to correctly analyze and diagnose the disturbances that occur during the operation of a blast furnace.

Work at the Tuyères.—Regular routine work at the tuyères consists of the maintenance of correct blast pressures, observation of the condition of the furnace, as far as this is discernible through the tuyères, and keeping the mouth of the tuyères unobstructed by slag accretions. Apart from this, close observation of the appearance of the tuyères in order to detect impending difficulties as soon as possible and intelligent cooperation with the other operators in combating and eliminating the difficulties in question also make up part of the duties of the operator in charge of the work on the furnace floor.

Clear and unobstructed tuyères, not too intensely bright, are indicative of perfect working conditions within the furnace. Glaringly white as well as slowly darkening tuyères, on the other hand, form just as certain indications of disturbances and impending difficulties within the furnace.

While the operators on the charging floor are in a position to forestall serious wall accretions by making it a practice at the beginning of each shift to drive steel bars at the four corners or the sides of the shaft as far down as the top of the jackets, loosening any wall accretions in the act of forming, furnace floor hands may avoid or, at least, minimize the danger of slag accretions on the hearth or around the tuyères by plunging steel bars through the open tuyères

right across to the opposite cooling jacket. If the progress of the steel bar is stopped by solid impediments such as hard slag ridges, etc., a fairly heavy hammer may be used to drive the bar across, thus perforating the accretions and permitting fresh hot slag to penetrate the solidified slag. In order to make sure that the opposite cooling jacket may not be mistaken for solid slag accretions, the distance between this jacket and the back of the open tuyère used for this purpose is marked on the steel bar with chalk. It is obvious that if accretions are thus found to be present, steel bars must be driven through them from all directions and at regular intervals, changing the charge compositions and adding heavy scrap iron or fluorspar—as the case may be—until the accretions have been dissolved by fresh hot slag. If it appears impossible to remove the crusts in this way, a number of straight slag charges mixed with about 9 per cent of coke and a few shovelful of fluorspar are given until the accretions have been eliminated.

A thin scale of slag, covering the mouth of the tuyères and transmitting bright spots of light, are no indication of impending difficulties, and it is only necessary in this case, to insert the poking rod once in a long while. If, on the other hand, heavy layers of slag cover part or all of the mouth of the tuyère, these must be removed as soon as formed to open the way for the blast. In many instances, this operation, if performed regularly, will suffice to keep the tuyères clear, a slight change of the blast pressure, or a decrease of the flow of water through the jacket surrounding the tuyère in question being required, perhaps, to correct the evil. However, if the darkening or blocking of the tuyères is caused by some more serious trouble, poking does not give satisfactory results, but will aggravate matters by causing the formation of heavy accretions or “noses.”

Before taking recourse to radical changes of charge mixtures, the removal of accretions in front of a tuyère is attempted by tying up the bag or—if rigid blast pipe connections are used—by closing the blast gate, the heat generated at the neighboring tuyères melting off the crusts.

If several neighboring tuyères are affected, it is necessary to tie them up one at a time.

A few shovelful of fluorspar distributed over the cold tuyères will also help to dissolve the accretions, while very satisfactory results are often obtained by sending down 100 or 150 pounds of metallic lead. Some metallurgists report good results with the addition of

a few heavy pieces of iron scrap. If fines have been present in the regular charges, these should be left out for a while, and coarse material be added exclusively until the difficulties at the tuyères have been overcome. If conditions do not improve after applying the above remedies, three or four straight slag charges, containing about 9 per cent coke and 1 to 3 per cent fluorspar, are given and the composition or size of the succeeding regular charges are altered according to circumstances.

Blast and Blast Producers.—It is obvious from the above that the amount and pressure of the air blast are of greatest importance in determining the smelting capacities of the blast furnaces, and the success of smelting operations generally. Too strong or too weak a blast will soon “kill” a blast furnace, the latter more gradually but just as surely as the former, especially if the lead blast furnace is operated with forehearth, where a certain speed of flow is required to supply the necessary heat to the contents of the forehearth.

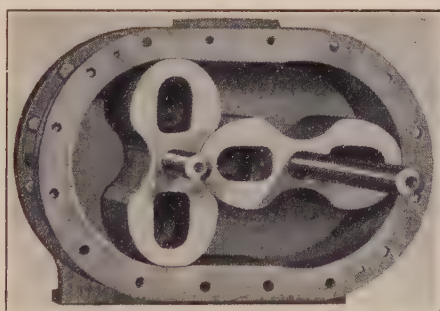


FIG. 33.—PUMPING ACTION OF ROOTS ACME ROTARY BLOWER.

Electric fans, while frequently used for supplying small lead blast furnaces with air, are inefficient and do not, as a rule, furnish sufficient pressure, and the only type of machines giving satisfactory service are the rotary-pressure blowers. Of these, the Roots blowers are most widely used in this country. A lead blast furnace of from 3 by 5 to 3 by 6 ft. requires a No. 6 blower.

The pumping action of the Roots Acme Rotary Positive Blower is easily understood from Figure 33.

Two impellers mounted on parallel shafts rotate in opposite directions. The relation of the impellers to each other is accurately maintained throughout the revolution by means of timing gears, one on the

end of each shaft. The shape of the impellers is such that during rotation there is a definite, accurately maintained clearance between impellers and case at all times. There is, therefore, no internal friction and no internal lubrication is required.

When an impeller is in the position in which one tip has just cut off the opening to the suction side, and the opposite tip is ready to leave the case so as to open to the discharge side, there is a volume of air trapped between the impeller and case which is not open to either the suction or the discharge. As the impeller continues to rotate, it opens to the discharge and pushes the enclosed volume of air positively into the discharge pipe. The action is repeated twice for a revolution of each impeller or four times for each revolution of the blower.

The practical advantages of the Roots Acme Blowers are:

1. They require no maintenance attention except occasional oiling.
2. Since there is no actual contact between the impellers and head plates or the impellers and the case, friction is practically eliminated at every point except, of course, in the bearings and gears.
3. Since there are no valves or restricted portways through which the air must pass, air friction within the blower is reduced to a minimum.
4. Roots Acme Blowers require no internal lubrication, they operate smoothly, and their simple and rugged construction insures efficient and dependable operation, as well as long life.

Figure 34 shows a Roots Acme Blower for belt drive with single pulley.

The pressure of the blast is usually measured by mercury or water gauges, 1 lb. pressure per square inch equaling 2 in. of mercury or 28 in. of water. For the small types of lead blast furnaces generally used for residue smelting, a blast pressure of from 20 to 25 in. of water is usually found satisfactory. Simple and efficient gauges are made by affixing a U-shaped glass tube to a thin board provided with an inch scale, which is connected with the air supply line by a short rubber hose. If water is being used as indicator, this is usually colored red to facilitate reading of the gauge.

Work at the Tap Hole.—The exact nature of the work at the taphole depends, of course, on the kind of tap used, that is to say, whether the blast furnace is supplied with internal crucible—with

or without Ahrents automatic tap—or if the smelting products are made to run into, and separate in, a forehearth. Internal crucibles provided with the automatic tap are not generally used in residue smelting lead blast furnaces, since in view of the comparatively small capacities and the large amounts of tin and antimony usually present in the metal produced, difficulties are usually more common and serious as in the case of the large ore blast furnaces producing relatively pure grades of lead.

Apart from the always present danger of freezing of the tap holes, internal crucibles possess the disadvantage of requiring constant attention and a considerable amount of “muscle metallurgy”; accretions are easily formed and hard to remove, and the poor accessibility of furnaces of this type make frequent blow-downs unavoidable. Thus, wherever lead blast furnaces with internal crucibles are still being operated, the most sensible procedure is to brick up the crucible and to continue operation with an open tap and a forehearth.

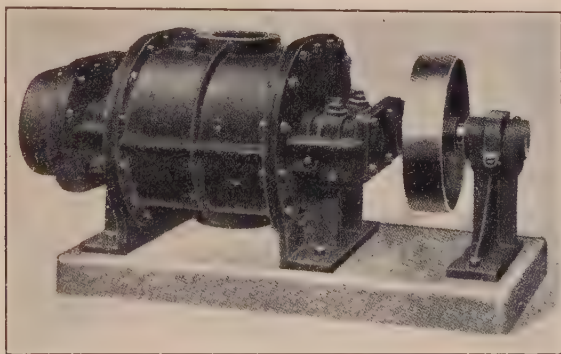


FIG. 34.—ROOTS ACME BLOWER FOR BELT DRIVE.

The operation of forehearths, with or without automatic taps, does not offer any appreciable difficulties unless the amounts of metal and slag produced are too small to keep the slag contents of the forehearth in a sufficiently fluid state. As a rule, that is to say, with a production of about one ton of lead per hour, a thin crust of frozen slag is formed on the surface of the bath of slag maintained in the forehearth, and this should not be disturbed by any means, since it represents a natural and most effective protection against the chilling of the fluid slag beneath. If the forehearth is operated with automatic tap, the work of the operators thus consists of keeping

open the blast furnace tap and the two holes in the cold slag cover, to replace filled slag pots with empty ones, and to ladle out the lead, rising up in the well, at certain intervals.

General Work at the Furnace Floor.—Aside of the work at the tap, or forehearth, and the tuyères, regular work on the furnace floor consists of wheeling the slag to the dump, piling the lead ingots upon the ground, or on trucks for removal, attend to the water supply, and of keeping the blast furnace in good running shape generally.

CHAPTER XIII

BLAST FURNACE COKE

The only fuel generally used for blast furnace operation is the smelting coke, although other fuels such as charcoal, coal, and even wood have been, and are still being, used for this purpose. Charcoal, alone, or mixed with coke, is often recommended for the smelting of tin ores and residues, while coal and wood are sometimes used in localities where on account of long transportation, etc., coke would represent too expensive a fuel. It is well known, for instance, that some of the first blast furnaces operated in the far West were fed with sawed off wooden logs, soaked for some time in milk of lime to prevent too rapid a combustion in the upper section of the shaft. According to rumors and reports emanating from Russia, wooden logs are still being used in blast furnaces in large parts of Russia.

Good blast furnace coke should possess the following properties:

1. It must be resistant to breakage.
2. It must be sufficiently strong and tenacious to resist the abrasive stresses to which it is subjected in the descending blast furnace column.
3. It must possess a high degree of combustibility.
4. The nature and degree of porosity must conform to the characteristic requirements of the blast furnace process.
5. The ash contents must be low.
6. The percentages of sulphur, phosphorus and moisture must not exceed a certain low maximum.

High resistance of blast furnace coke to breakage as well as to the compressive and abrasive stresses involved is the most important physical requirement made of blast furnace coke. This includes resistance to breakage during the transportation of the coke from the producer to the furnace, and resistance to compressive and abrasive stresses during the passage of the coke down the blast furnace shaft. The resistance to breakage is usually determined by the "Shatter

test," in which a 100 pound sample of coke, composed of pieces too large to pass through a 2-in. square mesh screen, is dropped four times onto an iron plate from a height of 6 feet, and the amount of coke which stays on the 2-in. screen noted.

The crushing stress imposed upon the coke by the weight of the charge column is very much overestimated as a rule, and the strength of an average grade of smelting coke will always prove sufficient to withstand the comparatively low crushing stresses imposed on the constituents of lead and copper blast furnaces.

Of greater importance is the resistance of the coke to abrasion. It is obvious that the changes of location of the individual pieces of coke and the other charge materials due to changing diameters of the shaft and unequal rate of descent will impose considerable abrasive stresses, which cause the partial crumbling of the coke before it reaches the zone of fusion. The weaker the coke, the larger the amount of coke fines produced and the more serious the difficulties due to the clogging up of the air passages and the increasing resistance of the fines to combustion.

The resistance of coke to abrasion is determined by the "Tumbler Test." A sample of about 100 pounds of coke, consisting of pieces large enough to remain on a 2-in. square mesh is tumbled in a barrel for a definite length of time, and a subsequent screen analysis gives a figure assumed to represent the friability of the coke. As a rule, it is required that at least 80 per cent of the coke must stay on a 2-in. square mesh screen. This test must be modified to apply to the various brands of coke.

The combustibility of blast furnace coke may be defined to mean the ease with which coke reacts either with air or with carbon dioxide under the conditions of the blast furnace process, although authoritative opinion on the definition of this term is all but uniform. While some authorities define combustibility to mean the rate of oxidation of coke by atmospheric oxygen, this term is also considered to mean the reduction of carbon dioxide by coke, or the ignition temperature of coke.

It is impossible here to go into details regarding the various academic points in question. Suffice it to say that a high degree of combustibility of coke is required:

1. To cause as rapid a conversion of the blast air into carbon monoxide as possible.

2. To further the different chemical processes involved in blast furnace smelting, within or directly above the zone of fusion.

The combustibility of blast furnace coke is closely related to the question of porosity, although the nature of porosity best suited to induce a maximum degree of combustibility represents another subject of considerable dissension among authorities such as Suthcliffe, Thau, Bunte, Fitz and Evans. According to Thau, the question of porosity is not to be confused with that of density, which is not an important factor in the consideration of the combustibility of coke. Very dense coke may indeed have a high degree of combustibility, provided the coke is free from impurities and that the cell structure of the coke is open. Thau points out that cells or "porosities" in coke that are visible to the naked eye do not determine the degree of reactivity, which is assured only if the tiny cells throughout the structure of the coke are open. If these cells are closed by slag, ashes, or graphite, etc., low combustibility is bound to result.

Investigators in general agree that the presence of large pores in blast furnace coke has no noticeable bearing on its combustibility, but that this property is indicated by a high degree of permeability of the coke to carbon dioxide and hydrogen. Suthcliffe and Evans¹ also believe that the type of porosity of coke required to induce a high degree of combustibility is not expressed by the presence of large, discontinuous pores as much as by interconnected pores.

The sulphur contents of blast furnace coke are not as deleterious to the smelting process in lead, tin, or copper blast furnaces as in iron blast furnaces or in cupolas. Washing the coal used for coking decreases considerably the percentage of sulphur present in the washed material. This is due to the fact that the sulphur is mostly present in the form of pyrites, which is much heavier than the coal, so that on washing the crushed coal the material rich in sulphur is settled out and separated.

¹ J. Soc. Chem. Ind. 41, 196 (1922).

CHAPTER XIV

THE REFINING OF SECONDARY WORK LEAD AND LEAD SCRAP

Practically all lead wastes and residues smelted in lead reverberatory or blast furnaces contain varying percentages of one or more impurities which, while eliminated to a greater or lesser extent in the preliminary smelting treatment, will reappear in the work lead subjected to the final refining process. For instance, no matter how much sulphur or sulphides present in the reverberatory or blast furnace charges, a certain percentage of copper will always contaminate the work lead, while even the zinc contents of residue and scrap material, the extraordinary affinity of which for oxygen is well known to every metallurgist, will not be entirely eliminated, if the furnace atmospheres are regulated with due regard to the main requirements of the smelting processes involved. Most of the tin and antimony contained in the raw materials, as well as a large proportion of the original arsenic contents will also contaminate the work lead, while practically all of the bismuth, silver, and gold, present in the lead residues treated will be concentrated in the soft lead produced.

Of these constituents, practically all the tin, antimony, and arsenic present are removed by scorification, copper may be eliminated to a large degree by segregation, while bismuth, the rest of the copper, silver, and gold, which are less readily oxidized than lead, remain in the refined lead and may be removed by a "zincing" process only. These elements may also be eliminated by the electrolytic and the Pattinson process, of course, but while the former cannot, for obvious reasons, be discussed here, the latter is incomparably inferior to the Parkes, or zincing process and need not, for this reason, be considered in connection with the refining of secondary work lead and lead scraps.

Refining Secondary Lead and Lead Scrap in the Melting Pot.—It has been indicated above that while the lead refining process really belongs to the sphere of the reverberatory furnace, it is quite possible

to refine impure lead in the melting pot. This fact is particularly important to lead working industries desiring to evaluate their own lead scrap, or to small residue smelters where financial considerations, or, perhaps, lack of space or sufficient quantities of raw materials, make the erection of lead reverberatory furnace uneconomical.

The field of application of the melting pot furnace for the refining of impure lead is of necessity a comparatively narrow one. Very impure work lead or lead scrap, particularly material rich in tin, cannot economically be refined in this manner, and only such raw material should be subjected to melting pot refining as do not contain more than 2 or, at most, 3 per cent of antimony and 0.25 to 0.50 per cent of tin.

Another factor of economic importance is the amount of impure lead to be refined, or the capacity of the melting pot furnaces selected for this purpose. Refining lead in small pots is absolutely uneconomical and inefficient, since the amount of labor involved is practically the same with small and large units, and since the ashes and slags produced in the refining treatment of small quantities of lead represent a prohibitive proportion of the amounts of lead treated.

Lead refining pots should therefore be large enough to hold at least 8 to 10 tons of lead, with about 10 in. to spare to allow for the agitation of the lead surface caused by the refining treatment. The most appropriate shape of lead refining pots are shown in Figure 9.

The melting pot units employed for this purpose should be supplied with steam and air pipes required to conduct the oxidizing agents into the lead. The steaming process has been described in detail on page 134.

The refining process is carried out as follows: Work lead and lead scrap are charged into the pot until this is filled up to about 10 in. from the rim. The temperature of the metal is then raised to red heat as rapidly as possible and steam and air forced through. If copper is present in the raw materials, the lead is melted down more gradually and a low temperature is maintained until the bulk of the copper present has settled out in form of a dross on the surface of the metal.

A few minutes after steam and air begin to pass through the bath, tin ashes commence to collect at the surface of the metal, oxidation growing more rapid as the metal gets hotter. The tin ashes are taken off regularly every 10 to 15 minutes. Gradually, the dry tin oxide will begin to show signs of "moistening," indicating the beginning

of the oxidation of antimony and the formation of liquid antimony slags. The elimination of antimony then proceeds until the dark brown antimony slag produced shows distinct signs of greenish yellow lead oxide contents.

Towards the end of the process, samples should be taken every 10 minutes in order to observe the progress of the refining process. In many smelters this test is carried out very roughly and inaccurately by pouring a small ladle of the metal on an iron or brick slab, the appearance of the extreme ends of the lead rivulets formed taken as indication of the state of purity of the metal. The following testing method avoids all the errors involved in the above primitive test, indicating the various stages much more accurately and clearly.

The metal is poured in sample molds consisting of a flat sheet iron box about 12 inches long, $1\frac{1}{2}$ inches wide, and $\frac{1}{2}$ inch deep. As long as an appreciable percentage of antimony remains in the lead, the surface of the test bar will be colored more or less grayish white, turning into a silvery white as this element is being eliminated. At the same time, the concave surface of the impure lead bar—at the front end—turns into convexity with increasing purity of the sample. The last stages of the processes are marked by the appearance of clear rainbow colors on the smooth and convex surface of the bar, showing first at the point where the stream of metal enters the mold, and gradually extending towards the other end. The refining process may be considered finished as soon as the fine crystal-lines visible at the rainbow-colored front end of the test bar disappear, while at the same time, the slag produced has turned completely yellow.

An impure lead material containing, say, 2 per cent of antimony and 0.2 per cent of tin, will, in a 10-ton pot and at good red heat, be refined within 8 to 10 hours. The lead contents of the refined product will be about 99.75 per cent. The further refining of the lead towards the production of a material of 99.93 per cent purity is achieved by zincing (page 202). The wear of the melting pots occasioned by the refining treatment of lead is not nearly as prohibitive as is often supposed, provided, the melting pot plant is tended with appropriate care. Ordinary cast iron refining pots will be able to stand about 75 to 90 charges, while steel pots, correctly treated can outlast 120 to 150 full charges of the common grades of impure lead.

Refining Lead in Reverberatory Furnaces.—While under certain conditions not altogether uncommon in small American and Euro-

pean residue smelters, the refining of secondary work lead and lead scrap may thus be considered economically and technically satisfactory, there can be no doubt that even comparatively pure lead materials are most efficiently refined in reverberatory furnaces wherever the financial position of the smelter and the available supply of lead scrap and residues justify the construction and operation of smelting units of larger capacity.

The capacity of lead refining reverberatory furnaces ranges from 10 to 250 tons, although very few residue smelters will take a chance at constructing furnaces larger than 30 or, at the most, 40 tons. Conditions in the lead and residue markets have never been stable enough to make larger smelting units a paying proposition, unless it is attempted to restrict the lead refining operations of the smelter to one furnace.

It may be considered a fundamental error, however, to rely upon the serviceability, or the "good behavior" of one refining furnace alone, since it is a peculiar experience of most metallurgists that single furnaces usually "go on strike" when the rush of orders is at its height. Wherever possible, two or three lead refining furnaces should be operated, even if the capacity of these furnaces does not exceed 25 tons. All lead refining furnaces are subjected to considerable wear, due to the characteristic properties of hot lead and the highly corrosive nature of the antimony slags produced, so that periodical repairing of hearth and walls of these furnaces cannot be avoided. It is self-evident, therefore, that since the furnaces will often require extensive repairing in times of pressing business, the corresponding decrease of output of refined lead will least affect the smelter operating a number of furnaces.

Another considerable advantage of the operation of several units of lead refining furnaces is the fact that, say, 3 furnaces of a capacity of 20 tons of lead each will produce more lead than a single furnace of a capacity of 75 tons. The disadvantages involved, that is to say, larger floor space requirements, higher costs of construction, and higher operating expenses, are not too considerable in view of the security from sudden interruption of production afforded by the operation of several units.

Construction of Reverberatory Furnaces.—The general principles underlying the construction of lead refining furnaces, being identical with those of practically all other large reverberatory furnaces, will not be described here, but it appears necessary for a clear under-

standing of the fundamentals of lead refining practice, to discuss those characteristic points of interest and the various important features of furnace construction which, directly or indirectly, influence the technical and economical success of the process involved.

One of the most outstanding factors determining the economic success of lead refining practice is the question of refractories most suitable for the construction of the hearth and the lower section of the walls. The fire-clay bricks used for this purpose for many years have gradually been replaced by magnesite bricks in a number of residue smelters, particularly in Central Europe. A careful study of this situation carried out by several metallurgists, including the author, in a number of European residue smelters showed, however, that in the majority of cases where fire-clay bricks proved to render unsatisfactory service, magnesite bricks were found to be but little better—in spite of their much higher costs—the few, very few, advantages possessed by these brittle and extremely sensitive refractories being outweighed by a startling variety of more or less serious disadvantages. It was also shown that in practically all smelters included in this survey the results obtained with magnesite bricks were not uniform, and it is obvious that the treatment accorded the furnaces during operation and idle periods possesses a higher degree of influence on the longevity of the furnace bottoms than the kind of bricks used. Another, equally important, factor is the method of laying the bottom and the preparation of the new bottom previous to taking the furnace into service.

Considering all the evidence gathered it appears, indeed, that the refractory, physical, and chemical properties of high grade fire-clay bricks are in no way inferior to the corresponding properties evidenced by the much more expensive magnesite refractories. A well burned, neutral fire-clay brick, free from excessive percentages of coarse silica grains is much more resistant towards the thermal stresses imposed on the furnace linings, and is not attacked, chemically nor mechanically, by metallic lead and dry oxides at any temperature involved in the refining of lead, while no kind of refractory material used in practical metallurgical work is able to stand up under the chemical or dissolving action of the antimony slag produced. The slight difference in the rate of corrosion suffered by magnesite and fire-clay bricks at the antimony slag level is hardly noticeable under actual working condition, while in a number of instances, fire-clay bricks proved to be the most resistant.

It is a generally recognized fact that the destruction of lead refining reverberatory bottoms is not due to any complicated physical or chemical actions of the hot metal, but simply to the high specific gravity, that is to say, to the lifting power of fused lead. Wherever the bottom of a lead refining furnace offers the slightest opportunity for the lead to penetrate into the lining, one or more of the bricks located near that leak are bound to make their appearance at the surface of the metallic bath within a short time, unless extreme care is paid to the laying of the bottom in such a way as to hold the respective bricks in position by sheer mechanical force. Correct curvature and closest possible joints will tend not only to lessen the possibility of the presence of weak points, but to counteract the lifting force of the lead penetrated into and under the hearth lining.

In view of the respective physical and technological properties of magnesite and fire-clay bricks, the latter are by far the most easily workable. They are readily cut into shape and rubbed into a close fit with the neighboring bricks, while a similarly satisfactory preparation of each individual magnesite brick is practically impossible. It is extremely difficult to chip off appreciable parts of the bricks without causing cracking of the glassy structure, and the hardness of the material prevents efficient grinding of the surfaces.

Thus, since it is practically impossible to effect sufficiently close fits and correspondingly close joints between the individual bricks composing the bottom of lead refining furnaces, magnesite bricks require the use of heavier layers of mortar, which are much less resistant to the penetrating action of the lead than the bricks. With the gradual removal of the comparatively heavy layer of mortar, however, the affected brick loses its contact with the neighboring bricks, while the entire series of bricks, making up the row in question ceases to be held in place and is brought to the surface of the bath in short order. This same difficulty does not exist where the bottom bricks are not laid in individual rows, but are interlocked in two or three rows.

With correctly laid fire-clay brick bottoms, washing out of small sections of thin layers of mortar does not cause the floating of the affected brick which are held in place by the close fitting rows or series of rows interlocked with each other.

Another very serious disadvantage of magnesite bricks is their low degree of resistance against sudden changes of temperatures.

It will be shown on page 277 that of all the refractories used in common metallurgical practice, magnesite bricks exhibit the lowest resistance to abrupt temperature fluctuations. Table 41 shows the relative resistance of the various kinds of refractory bricks compared with magnesite bricks, the value 100 indicating the minimum resistance.

The formation of dangerous cracks in magnesite bottoms can therefore be avoided only if furnace and bottom are treated with utmost care, especially throughout the first two or three months of active service. It is practically impossible, of course, to constantly maintain ideal working conditions in ordinary smelting operations, so that, considering all factors, fire-clay bricks will doubtlessly give best results in the long run. A well constructed bottom built up of perfectly burned, basic fire-clay bricks will easily last one year and is very much cheaper than magnesite bricks.

Wherever magnesite bottoms are used, furnace temperatures must be maintained as constant as possible. Temperature changes in either direction must be effected with due consideration to the lack of resistance against temperature fluctuations characteristic of magnesite bricks. On cooling down the furnace, all working doors, firing and ash pit door, as well as the blast air openings should be closed tightly and the draft shut off. Before closing up the furnace hermetically, the hearth should be covered with a heavy layer of coke fines. If for better protection of the magnesite bottom a layer of lead is maintained in the furnace—by placing the tap hole a few inches above the center line of the hearth—this layer of coke fines will still prove advantageous; retarding as it does the rate of cooling of the lead. With fire-clay bottoms this additional precaution need not necessarily be taken, of course, although the longevity of these bottoms is also increased by the lead blanket.

Cooling Jackets of Lead Refining Furnaces.—Another factor of considerable importance in the operation of lead reverberatory furnaces is the cooling of the furnace walls at the antimony slag level.

It is understood, of course, that in view of the considerable thickness of the furnace walls, the cooling jackets cannot be expected to prevent corrosion entirely, the cooling effect being limited to a certain retardation of the rate of corrosion only. The corrosive action of the hot antimony slags causes the gradual solution of the walls at the slag level until the thickness of the remaining brickwork amounts to about 7 or 8 in. At this point, the protective action of the cooling

jackets becomes effective, and instead of further corroding the walls, the antimony slag touching the cooled sides commences to solidify, forming a natural protection against further corrosion.

The rate of corrosion effected by the antimony slags is governed by the following factors:

1. The amount of antimony contained in the lead.
2. The speed of oxidation.
3. The force of the blower.
4. Direction of the blow-pipe.
5. The average heat maintained.
6. Thickness of walls.
7. Quality of the refractories employed.

The importance of points 1, 2, 5, 6, and 7, is self-evident. The effect of the force of the blower and the direction of the blow-pipe is due to the lesser or higher degree of disturbance of the metallic surface of the metal. With a strong blast and if the blow-pipe is directed diagonally against the lead surface, waves are produced which are radiated across the entire surface of the bath, causing the antimony slag to be washed against the walls of the furnace continuously, and it is obvious that this action will effect a higher degree of corrosion than an unruffled slag layer.

It is a mistake to assume that the corrosive effects of the hot antimony slag cannot be counteracted by cooling, and that at sufficiently high furnace temperatures this slag would be corrosive enough to pierce the cooling jackets. If an iron tube connected with the regular water supply is stretched through the furnace, well in the antimony slag line, permitting a heavy layer of white hot antimony slag to act on it for a number of hours, it will be found that the water-cooled tube will not show the slightest indication of corrosion, a heavy layer of solidified slag, formed around the tube almost immediately, preventing any direct contact between the iron and the active antimony slag.

A very simple but absolutely effective method of neutralizing the corrosive effect of antimony slag on the walls of lead refining furnaces is available where, apart from the antimonial lead treated, scrap lead poor in antimony but comparatively rich in tin is to be refined. If after a certain period of refining of antimonial lead the furnace walls have gradually been hollowed out about 4 or 5 inches, a number of

charges of the other lead material containing tin are subjected to a slow refining process, that is to say, without the application of blast air. If the metal surface is then made to fluctuate up and down near the former antimony slag level it will be found that the affected sections of the walls are gradually filled up by tin oxide-slag mixtures, which are much more resistant to the corrosive action of antimony slags than any refractory material available.

Experiments carried out to determine the relative resistance of various brands and grades of fire-clay bricks have shown that this property is but little influenced by the respective alumina contents of the refractories, bricks containing only 25 per cent of alumina standing up as well as others analyzing 30 or even 35 per cent alumina. It is a peculiar fact, however, that light and soft, porous, bricks are distinctly more resistant than the dense and strongly burned varieties.

The cooling jackets may be made from either cast iron or wrought iron, if these are located at the outside of the furnace walls, and if the slag is not permitted to approach within less than 10 inches. Wherever the antimony slag is suffered to penetrate deeply into the walls, or where the cooling jackets are located within the wall, the thickness of wall between jackets and active slag being decreased to considerably below 10 inches, cast iron jackets are not proof against the development of cracks, giving rise to explosions, etc., and wrought iron cooling jackets should therefore be used in these cases.

The Air Blast System.—Considerable divergence of opinion still exists concerning the methods of oxidation, or scorification, of the various impurities of the lead. A number of lead refining plants do not make use of the air blast at all, others apply the air blast throughout the entire refining process, while many smelters combine both systems by working without blast during the first part of the process, that is to say, throughout the tin oxidation period, applying the blast and speeding up the refining operations as soon as antimony slag commences to be formed.

The chief arguments advanced against the use of the air blast are:

1. The tin contents of the tin ashes formed are considerably lowered by the rapid oxidation of the metal induced by the blast.
2. The corrosive effect of the antimony slags on the furnace walls is appreciably increased by the agitation of the metallic surface.
3. The introduction of a strong blast of cold air tends to decrease the furnace temperatures and lowers the heat efficiency of the furnace.

The most obvious advantages of the application of the air blast in lead refining appear to be the following:

(a) Oxidation of the impurities and, therefore, the speed of the refining process are improved by several hundred per cent.

(b) Removal of the slag formed is considerably facilitated. While, in the first place, the blast directed down against the surface of the metal will force the slag back towards the opposite end of the furnace, constantly exposing part of the metal surface to the direct action of the air and concentrating the slag within the other section, the cold air causes the antimony slag to flow viscous, thus facilitating its removal through the slagging aperture.

It is evident from the above that this problem, like many others, cannot be solved by fixed rules, but that the question of working with or without air blast must be decided by the various conditions obtaining in each and every case. It appears, however, that in view of the variety of raw materials treated in practically every commercial residue smelter, mixed operation is the only economical solution. Since in treating lead materials high in tin, best results are obtained if the tin ashes are maintained at as high a tin content as possible, oxidation of this constituent should be effected as slowly as is compatible with the maximum time permissible. If the metallic bath is subjected to the action of blast air at this period, the tin ashes obtained will rarely carry more than 10 to 12 per cent of tin, while if operating without blast and generally retarding the process of oxidation, tin contents of more than 30 per cent are easily attainable.

The same is true of the antimony contents of the antimony slags, which are bound to be considerably higher if oxidation is left to a strongly oxidizing furnace atmosphere alone. However, while in the case of tin, the loss of time accrued may be considered justifiable by the correspondingly higher values of the tin ashes produced and the more complete separation, or concentration, of the tin into one product, it may well be doubted whether an increase of the antimony contents of the antimony slag by not more than 50 per cent will justify the lengthening of the refining process by at least 100 per cent. For instance, while a 25-ton charge of antimonial lead, containing, say, 6 per cent of antimony will, by making use of the air blast, be charged, refined, and tapped within 24 to 30 hours, refining of a similar quantity of the same lead and under the same conditions, but without air

blast, cannot be accomplished within less than 60 to 75 hours. If it is considered that during that time the furnace must be constantly tended by at least one man, and keeping in mind the additional amount of fuel required as well as the greatly increased wear of the furnace per ton of lead produced, the economical value of slow refining as applied to the antimony contents is indeed doubtful.

It is understood, of course, that the average time required for the refining of lead without air blast may be appreciably shortened by suitable construction of the lead refining furnace, that is to say, by providing for a favorable surface area-volume ratio. The larger the surface of the metallic bath the more rapid the oxidation per unit of volume, although, apart from the larger floor space required and the higher initial costs of construction involved, the concentration of the products of oxidation will also be decreased somewhat. Thus it appears that for all general work, secondary work lead and lead scrap containing appreciable quantities of tin and/or antimony are most economically refined by applying the air blast after complete elimination of the tin, and throughout the entire antimony oxidation period.

In using the air blast, really satisfactory results can only be obtained if the force of the blast is sufficiently strong, and the direction of the air current sufficiently oblique to cause proper agitation of the metallic surface without throwing up a spray of lead, thus forcing back the slag towards the opposite end of the furnace and exposing part of the metallic surface to the direct oxidizing action of the blast. As a rule, the air is introduced through two sheet iron tubes passed into the furnace through narrow openings in the narrow firing side. It is then possible to use part of the blast air as "secondary air supply" to complete the combustion of the oil or gases, while, as a second advantage, the slags are driven towards the cooler end of the furnace, thus facilitating their removal by means of wooden skimmers. The chemical and mechanical effect of the blast is greatly improved by flattening out the mouths of the tubes, projecting flat, sharp blasts upon the surface of the metal.

The Tap Hole.—In view of the strongly penetrating action of hot lead, due attention must be paid to correct construction and operation of the tap of lead refining furnaces. The disadvantages of the slit type of taps, which on account of the characteristic chemical and physical properties of lead are particularly in evidence in lead refining practice, preclude it for this purpose, while bottom taps are

satisfactory only if cooled sufficiently to permit of the use of wooden plugs instead of the clay plugs frequently employed.

Cooling of the tap may be effected by open or closed water jackets specially constructed for this purpose, and surrounding the tap hole on all sides. However, it is absolutely necessary in this case to cool the tap separately, since a connection of this section with the general cooling system would not provide the tap with sufficiently cold water to prevent accidents.

The use of efficient cooling systems, besides preventing sudden breaks, permits of the employment of the only efficient plugging medium, wood, which previous to charging the furnace is hammered deeply into the tap, while tapping of the lead is effected by simply piercing the plug with a red hot iron rod. Many years of experience have not brought to light one single instance, where a wooden plug, correctly hammered into the tap hole, and efficiently cooled, had been penetrated and pierced by the red hot lead, although in many instances, that is to say, in treating 100 ton charges without the application of blast air, refining periods averaged higher than one week.

The most effective, though primitive, method of tap-cooling observed by the author in some Continental lead smelters consists of moistening the outside of the tap by means of a fine stream of cold water directed against the wooden plug by a thin copper pipe connected directly to the water supply. The excess water trickles down to the short spout and is conducted into a wide drain-funnel. Shortly previous to tapping, the water is turned off, and the spout and tap section is dried carefully by placing a few shovelful of glowing coke on the spout. Connection between the spout and the fore-kettle is then made by means of a U-iron or a similar contraption lined with fire-clay. It is obvious that a break of the red hot lead through a tap cooled in this manner is practically impossible. The device is simple, inexpensive, and fool-proof.

The Refining Process.—Work lead produced from lead residues usually contains copper, tin, antimony, zinc, and, sometimes, arsenic. All of these impurities, with the exception of bismuth, may be removed by fire refining, that is to say, tin, arsenic, and antimony by oxidation, or scorification, copper by segregation and zincing, and zinc by volatilization. If, in presence of the precious metals, gold and silver, zincing follows the furnace refining process, the small quantities of impurities remaining in the lead are reduced to traces at the same time.

The process is carried out as follows:

The work lead, together with the various kinds of lead scrap suitable for direct refining, is charged into the furnace, the temperature of which at this point should not average higher than about 900° Fahr. It is just as well, however, to maintain a temperature only high enough to fuse the metal charged. After filling the furnace, this low temperature is retained for at least 3 or 4 hours, when all the dross formed on the surface of the metallic bath, containing the bulk of the copper present in the raw material, as well as some antimony, tin and lead, is taken off by means of perforated ladles.

The proper time allowed for the segregation of the copper dross is governed by the size of the charge, percentage of copper, tin, and antimony present, amount of zinc contained, and speed of charging. Since most of the copper dross obtained is doubtlessly separated out during the melting period, the method of charging represents a very important factor, influenced, of course, by the furnace temperatures maintained during charging. The effect of the zinc contents on the degree of separation of the copper is obvious, since next to gold, copper possesses the most pronounced affinity for zinc. In accordance with the principles of the Parkes process, sufficient zinc contents will cause the separation of practically all the copper, although this separation is interfered with by high tin and antimony contents. If silver and/or gold is also present in the work lead, appreciable amounts of zinc should not be tolerated, since the drosses formed will contain the bulk of the precious metals contained. However, since secondary work lead has almost invariably been produced by blast or reverberatory furnace processes, the percentages of zinc still remaining are practically negligible, so that serious amounts of zinc can only be introduced with the scrap.

The influence of tin and antimony contents on the separation of copper by drossing is due to the alloying propensities of these constituents, which, if present in appreciable amounts, will hold a corresponding quantity of copper in solution. This deficiency is easily made up, however, by finishing the refining process with a sulphurizing treatment, that is to say, by adding small quantities of lead sulphide ores and thoroughly rabbling the metal. A considerable percentage of the copper remaining is thus removed in form of matte. The addition of zinc to the red hot lead for the same purpose is futile, of course, since this is simply burned off, the small quantities

of metallic copper separated by the zinc being returned to the lead. If it is desired to remove practically all the copper remaining in the refined lead, this can only be accomplished by zincing in the iron or steel kettles used as forehearth after the temperature of the lead has been reduced to about 1000° Fahr.

Instead of the segregation of copper in the lead refining furnace proper, some authorities, such as Schnabel, recommend separate drossing or segregation in special furnaces, where the solid work lead is subjected to minimum segregation temperatures, most of the copper present being left behind as dross. This process is still in use at the Hoboken Smelter in Belgium (1923), but appears to be absolutely inefficient or, rather, uneconomical under the conditions prevailing in residue smelters, excepting where extraordinarily high copper contents are encountered and where a rush of orders and limited furnace capacity does not justify the loss of a number of hours involved in drossing out the copper in the lead refining furnace proper.

The amount of copper contained in the drosses is determined by various factors and ranges from 5 to 15 or more per cent, the bulk of the metals consisting of lead, with varying percentages of tin, antimony, arsenic, iron, zinc, and, eventually, silver, cobalt, and nickel. Gold, bismuth, and cadmium is not, as a rule, taken up by the dross.

If, on account of very high percentages of copper in the work lead, the amount of dross formed is considered excessive, it may be appreciably reduced by the addition of lead sulphide ores, which are shoveled in with the pigs and cause partial sulphurization of the copper. Since the affinity of copper sulphide for metallic constituents, such as antimony and tin is comparatively low, the dross obtained will be materially richer in copper and correspondingly more free from other metallic constituents. Another decided advantage of the presence of sulphur in the dross is the fact that if for some reason, the furnace temperatures are permitted to climb too high, the tendency of the copper to redissolve in the lead is considerably decreased.

The refining period proper is initiated by raising the furnace temperatures to about 1800 to 1900° Fahr. The gases of combustion are then rendered decidedly oxidizing and one or two working doors opened to permit free access of the air. Yellow tin ashes commence to separate out within a short time. The first tin ashes or crusts formed are always comparatively rich in tin, the exact percentages depending upon the percentage of tin contained in the lead bath and

the speed of oxidation, but reaching 30 to 45 per cent if the process is carried out correctly.

Gradually, the whitish yellow color of the tin ashes is changed into darker tints, while the consistency of the material changes from a dry and powdery state into a pasty, slaggy condition. This second product, consisting of dark yellow, heavy, granular crusts contains appreciably higher antimony contents, ranging from 3 to 5 per cent, and must be treated separately, the first product being reduced with solder ashes and similar material to form lead-tin alloys comparatively free from antimony and other materials.

Towards the end of the tin separation period, the tin crusts become increasingly richer in antimony and, eventually, arsenic, and the lead bath commences to give off heavy fumes of antimony and arsenic. If much arsenic is present, a certain excess will separate out in form of lemon yellow to light brown fused arseniate of lead. Soon, however, arsenic and antimony slags are formed together, the first antimony slag skimmings containing certain percentages of arsenic as well as tin, while it is hardly possible in presence of considerable percentages of tin in the charges to obtain antimony slags free from tin at any time until the slags commence to become contaminated with litharge, indicating the approaching end of the refining process.

Since it is practically impossible to facilitate the skimming of the antimony slag, which at the temperatures of the process is absolutely liquid, by cooling down the furnace, in order to harden the slag, and since even the introduction of the air blast and skimming at the coolest end of the furnace will not decidedly improve the skimming properties of this material, it becomes necessary to select skimming methods best adapted to remove the liquid antimony slag from the furnace.

The best skimming tool in the author's experience consists of a long heavy iron rod bent to a hook at one end, which is hammered into a round or square log of wood about 5 to 7 inches in diameter and long enough to just pass through the skimming door. This tool is used in connection with another appliance, also consisting of a bent iron rod and a wooden log of about the same diameter, but at least twice as long. While the log of the skimmer proper is affixed at right angles to the iron rod, the second is fastened in parallel with the rod in order to permit of sidewise skimming. Thus, while one man operates the first skimming tool at the skimming door, a helper, introducing the second skimmer through another working door, pushes

the antimony slag, collected on the surface of the metallic bath, towards the skimming end, so that the full amount of slag collected every 30 minutes may be removed within a few minutes.

The skimmed slag should not be run into sand or into shallow beds made up by piling sand around the edges of steel or iron plates since, apart from the danger to the operators introduced by the explosive and heat-preserving nature of antimony slags, much metallic lead is held by the slag. The only efficient method of collecting the skimmed slag is to run it over an overflow pot into slag pots, the bulk of the lead pulled out of the furnace together with the slag being collected in the first pot. The small amount of lead carried over into the cone-shaped slag pot is recovered on emptying the cooled pot. In applying this method, the slag should be skimmed in as liquid a condition as possible.

Various methods have been suggested to accelerate the oxidation of antimony and to prevent too strong an oxidation of lead. Earlier writers, as, for instance, Percy, recommended the treatment of the metallic bath with chemical oxidizing agents, particularly the nitrates and higher oxides of the alkaline metals. It is obvious, of course, that the disadvantages incurred by the application of such "metallurgical tricks" are bound to surpass considerably the meager advantages attained. The only practical method to hasten the process of oxidation is the addition of litharge, derived from some other metallurgical process, which is spread over the surface of the metallic bath well towards the end of the process. If this material is thrown on the clear lead surface—freed from antimony slags—the oxidation proceeds almost spontaneously, an oily-looking layer of antimony slag appearing directly after the addition of the litharge. If compressed air is introduced into the furnace during this stage of the process, the blast should be stopped until all the litharge added has been dissolved in order to prevent blowing most of this material into the flue dust. The author has also used accumulator plates with full success, the very small percentages of antimony contained in this material being negligible, especially since this will hardly be able to contaminate the lead bath, being the first antimony to be oxidized by the peroxide constituting the accumulator plates. Accumulator mud should not be added, however, since the impurities contained in this material, especially the acid, tend to influence the process unfavorably.

The progress of the refining process may be closely followed by the appearance of the products of oxidation formed, although fully

satisfactory results are only obtained if the work is controlled by the sample test described on page 188.

Tapping the Lead.—On reaching the degree of purity required, the surface of the lead is skimmed free and a few shovelful of coke fines distributed to prevent further oxidation of lead. The air blast and firing is then stopped and all the working doors opened wide. Tapping is delayed until the metallic bath has cooled down to dark redness. Two or three hours previous to tapping the forehearth kettles are heated up sufficiently to avoid cracking by the hot lead. A piece of strong sheet iron sufficiently large to cover the entire bottom of the kettles is then placed into each pot to protect the bottoms against the corrosive effects of the heavy streams of red hot metal. If the tap hole is placed directly at the bottom, the furnace must be permitted to empty entirely, and the tap hole as well as the neighboring section of the furnace bottom cleaned carefully before closing the tap, since the very last portions of metal leaving the furnace are contaminated with the remainders of slag, lead oxide, and coke fines, which in collecting and solidifying around the tap will seriously interfere with the subsequent opening of the tap hole.

The softened lead in the kettles is left to stand quietly for about half an hour to permit perfect separation of the metallic and non-metallic impurities carried out of the furnace.

In selecting the most efficient pouring methods to be adopted in each and every individual case, it should be remembered that the various mechanical pouring methods suggested and devised will prove efficient only if the amount of metal treated exceeds certain minimum quantities. A uniformly high degree of pouring efficiency can only be attained, however, if the construction of the entire lead refining plant, including the lead blast furnaces, is based upon the principle of gravity production, that is to say, the placing of the various units of the plant on various levels. Thus, if the lead refining furnace is built on a level about six to ten feet above floor level, the bottom of the melting pots, the rim of which is slightly below the level of the tap hole, will be approximately two to six feet above floor level, so that the lead may be poured by gravity, applying the ordinary syphon principle.

Zincing Refined Lead.—It is practically impossible by fire-refining methods to produce a refined lead product containing more than 99.75 per cent of lead from ordinary secondary work lead or lead scrap. Where purer grades are to be produced, it is necessary, therefore, to

subject the fire-refined lead to a zincing process which, apart from eliminating all the copper, silver and gold, will reduce the antimony, arsenic, and tin contents to minimum percentages. The only exception to the rule is bismuth, which cannot be removed by zincing. If in view of the high price of bismuth, extraction of this metal promises to be a paying proposition at all, application of a suitably modified variation of the Pattinson process alone would achieve the purpose.

Since the precious metals, silver and gold, are rarely present in residues of this nature, they will not be considered here. This subject is treated, in a special chapter on the desilverization of lead.

If the refining process proper has been carried out correctly, the amounts of copper, tin, antimony, and arsenic remaining in the refined lead should not exceed a total of 0.25 to 0.30 per cent, and one per cent of zinc should therefore be sufficient in practically all cases to produce a lead of approximately 99.93 to 99.96 per cent purity. Old common zinc scrap must not be used for this purpose, however, since the presence of more than 2 per cent of impurities in this material, especially the high percentage of tin always present, seriously deteriorates the zincing capacity as compared with that of comparative pure zinc. It will be found economical for this reason to provide for a small stock of clean sheet zinc scrap free from soldering seams.

This zinc should not be added until the temperature of the lead in the kettles has decreased to about 1000° Fahr. in order to avoid burning of a large part of the zinc added, particularly if this consists of sheet scrap. Stirring in the zinc by hand is antiquated and inefficient, and should be replaced by mechanical stirring. Mechanical stirring is complete after about 10 minutes.

Zincing may also be effected by steaming, a process which may prove efficient wherever economic reasons forbid the installation of mechanical stirring devices. It is important to keep in mind, however, that the effect of superheated steam varies greatly in accordance with the temperature of the lead-zinc mixture, and efficient stirring is possible only at temperatures of from 825 to 850° Fahr. Below that temperature, that is to say, about or below the melting point of zinc, a zinc crust is formed which contains only small percentages of the impurities to be removed. At much higher temperatures, commencing with dark red, a scum is produced which contains chiefly lead, the percentage of zinc present rarely exceeding 3 per cent, while the action of the zinc on the impurities of the lead is practically nil.

Steaming is carried out by means of the device described on page 134, steaming periods ranging from 30 to 45 minutes. While a certain small amount of zinc is oxidized in all zincing processes, this loss is highest with steam stirring, and small amounts of aluminum are usually added to the zinc to decrease or eliminate oxidation of the zinc.

After stirring, the lead is permitted to stand quietly for about 30 minutes at a temperature of approximately 750 to 800° Fahr. when the crust is removed by means of perforated skimmers.

The lead is then brought back to dark redness and the zinc remaining in solution with the lead is removed by steaming.

The resulting lead is thus brought up to a purity of 99.94 to 99.96 per cent, which is but little improved upon by a second zincing process. The expenses incurred by two zincing treatments would prove to be exorbitant in any case.

If the original refined lead is comparatively pure, the zinc crust obtained from one treatment may be used over again for the next charge, although it is necessary in this case to use a zinc containing a small percentage of aluminum to prevent excessive loss of zinc by oxidation.

The Desilverization of Refined Lead.—It has been pointed out that secondary lead bearing materials, especially the various kinds of lead scrap, drosses and ashes commonly handled by residue smelters, rarely contain silver or gold in sufficiently large quantities to pay for their extraction. It is often claimed that a considerable portion of the lead produced within the Central European countries during the World War contained appreciable percentages of silver, a fact said to be due to the excessively large demand for lead made upon the producers by the military authorities, which forced the smelters to carry out the desilverization of their virgin lead with less than usual care. This claim has never been substantiated, and the author, who has refined thousands of tons of scrap and residue lead in German smelters, has never been able to find paying quantities of silver in any of the materials treated.

However, residue dealers will sometimes come across smaller or larger lots of silver bearing residues usually shipped from Mexico, Peru, etc., and a number of other countries where the advancement of the metallurgical arts has not been equal to the silver contents of their ores, or where the residues in question represent picked sections of ancient smelter dumps. Thus the author has had occasion to treat

several hundred tons of Mexican lead ore residues containing 15 per cent of lead and as high as 7 to 12 ounces of silver per ton. There are reputed to be many hundreds of tons of argentiferous lead residues piled up in the close neighborhood of Guanajuato, Mexico.

In view of the relatively small importance of the desilverization process in scrap and residue treating works a short outline will suffice for the purposes of this volume. Readers desiring a more detailed discussion of this subject are referred to the various large publications on the treatment of lead ores.

Of the various processes suggested and applied for this purpose the so-called Parkes Process alone is almost exclusively used, although electrolytic processes of recovery of the silver in refined lead have also been introduced during the last 10 years. The Parkes process is based upon the fact that zinc possesses a higher degree of affinity for silver than for lead, and that the silver-zinc alloy formed is practically insoluble in lead saturated with zinc. The crust obtained is concentrated by liquation, the concentrates or "dry crusts" are subjected to distillation to remove the zinc, while the rich silver-lead alloy resulting is then subjected to cupellation.

Zincing is carried out as follows: The red hot lead tapped from the softening furnace is permitted to cool down to about 1050° Fahr., and the dross formed on the surface of the metal taken off by means of long-handled skimmers. The first half of the total amount of zinc required is then added and stirred into the metal bath, mechanical stirring giving by far the best results. Stirring with steam at certain fixed temperatures may also be applied, but this process has long since been abandoned in favor of mechanical stirring. The metallic mixture is then left to cool down to about 750° Fahr., and the crust removed by means of skimmers and charged into liquating kettles situated within a foot or so of the zincing pots. Figure 36 shows the arrangement of pots and liquating kettles best suited for this purpose.

A second and, if necessary, third charge of zinc is then added and the process repeated as outlined.

Liquating the crust obtained is accomplished by heating the kettle to a temperature of from 1200 to 1300° Fahr., gradually increasing the heat to about 1400° Fahr. until the kettle is filled with alternating layers of crust and charcoal. The kettle is then covered in order to prevent loss of heat and the excess lead contained in the crust permitted to drain into the iron pot placed under the tap hole as shown in Figure 36.

The dry crust obtained, the silver contents of which range from 2 to 7 per cent, is now subjected to distillation to remove the zinc, the silver being concentrated in the lead contents.

Distillation may be carried out in Faber du Faur retort furnaces or in reverberatory retort furnaces. The former give best results with small quantities of material and periodical operation, the latter are best suited for continuous treatment of large quantities of crust.

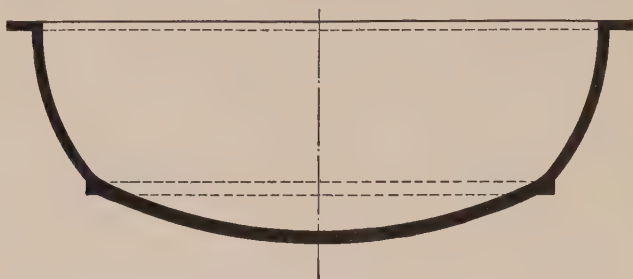


FIG. 35.—DESILVERIZING KETTLE.

Figures 13 and 14 illustrate the construction of distillation furnaces of the reverberatory type and the arrangement of the retorts.

The distillation process proceeds as follows: The dried crust is reduced to about walnut size, the bulk of the material being present in a more or less disintegrated state. This product is mixed with about 3 per cent of charcoal or reducing coal and charged by means of small elongated scoops or shovels. If the distillation is carried out in

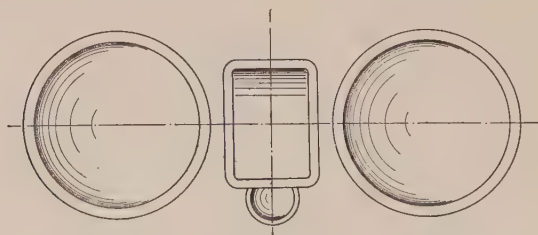


FIG. 36.—ARRANGEMENT OF DESILVERING PLANT.

Faber du Faur furnaces, the first charge is melted down rapidly at a temperature of 2000 to 2200° Fahr. and more charge added until the retort has received its full charge. In the case of reverberatory retort furnaces only one charge is given, but the material is pushed back and the retort filled to capacity. It is then closed by means of

a flat fire-clay brick, the surrounding spaces being closed with fire-clay mortar. A large opening at the top is left for the escape of the zinc vapors into the condensation chamber. This is then closed the same way, although instead of the large opening, a fire-clay pipe of about $\frac{1}{2}$ in. diameter is provided near the roof of the condensation chamber to permit of the escape of excessive pressure within the system. The small quantities of zinc vapor escaping through this pipe are conducted into a sheet iron "allonge" where it is collected in a finely divided state generally known as "blue powder." The products of the distillation process are:

1. Lead-silver alloy—retort bullion—containing from 4 to 11 per cent silver and from 1.0 to 2.0 per cent zinc, while the most common impurities are copper, arsenic, antimony, and bismuth.

2. Metallic zinc, about 10 per cent of which is obtained as blue powder. This zinc may contain from 0.25 to 0.30 per cent lead and from 4 to 15 ounces of silver, depending upon the rate of distillation and the richness of the zinc-crust.

3. Residues consisting of the infusible components of the retort charges and lead, the latter containing approximately the same percentage of silver as the retort bullion. About 80 per cent of this silver are usually extracted by treatment with softened lead bullion.

The rich lead bullion obtained from the distillation process is now charged in the cupellation furnace where the lead is removed by oxidation to litharge, while the silver is obtained as impure silver bullion.

Of the two standard cupellation processes formerly employed, the English and the German process, only the improved English cupellation method is applicable to residue smelter conditions. This process is carried out in small reverberatory furnaces with movable and removable hearths. The rich lead bullion is charged gradually—in contrast to the German process—and operations are practically continuous. Figures 37 and 38 show the construction of a modern English cupellation furnace.

The furnace consists of the fire-box heated by oil, gas, or coke, the movable hearth, known as "Test," which is supported on a truck, and the flue, the correct construction of which governs the efficiency of the process. Instead of making the truck a fixed part of the test construction, its use is often limited to transporting the test in and out of position, while during operation the test is supported on two horizontal beams laid at one end on a square bearing bar, and hung

from chains or jackscrews at the other. The test consists of an oval or rectangular test ring, enclosing the hearth made of a mixture of

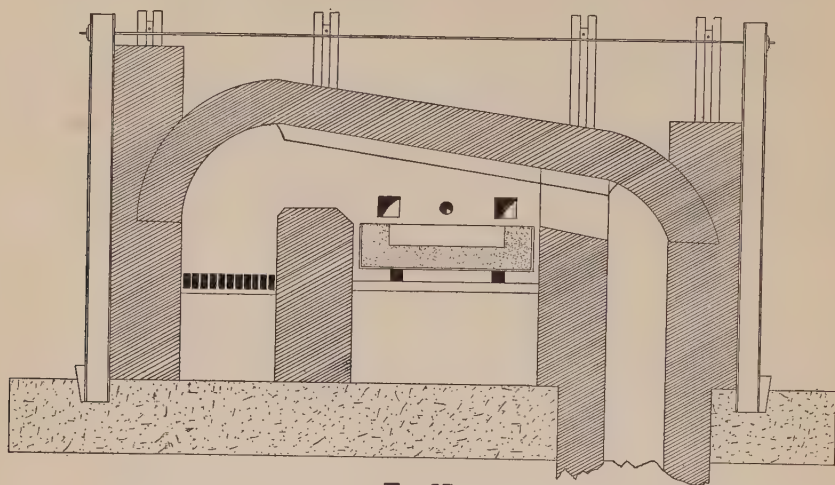


FIG. 37.

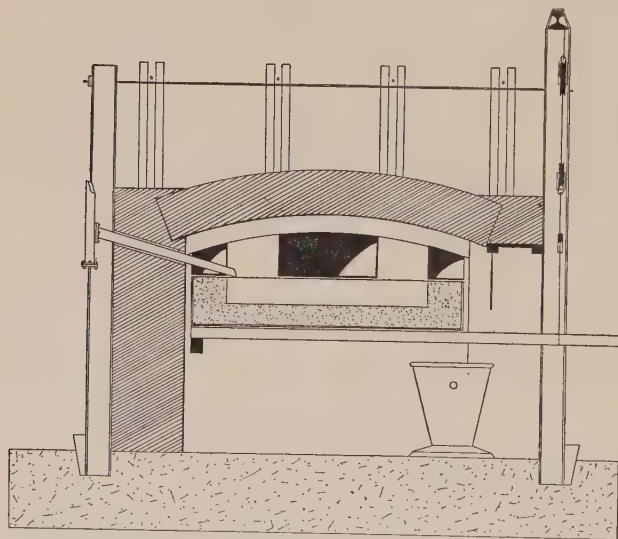


FIG. 38.

FIGS. 37 AND 38.—ENGLISH CUPELLING FURNACE.

cement and slag and resting on a cast iron plate. The hearth material most generally used in this country consists of a mixture of 6 parts

of limestone and 1 part of clay. Mixtures of Portland cement and ground fire-clay brick, or of Portland cement and slag are also being used, the latter mixture being most commonly employed in Europe.

The cupellation furnace is operated at a temperature of about 1900° Fahr., that is about 100° Fahr. above the melting point of the litharge formed. The ingots of rich lead bullion are charged through the opening provided in the furnace wall opposite the litharge channel cut across the front side of the test to allow the litharge formed by the oxidation of the lead to flow away into cast iron pots. The blast air is introduced through tuyère pipes led through two openings provided at the sides of the charge opening. Fresh lead bullion is added from time to time to keep the level of the bath as constant as possible, while the force of the blast and the flow of the litharge are regulated so as to keep about one half of the surface of the metal covered with the molten oxide. If too much of the metal surface is exposed to the oxidizing action of the blast, excessive quantities of silver are taken up by the litharge, while still more of the silver and lead is lost by volatilization.

Towards the end of the process, when the lead-silver alloy becomes sufficiently rich in lead to raise the melting point to nearly that of silver, the temperature has to be raised accordingly. The end of the cupellation is indicated by the "brightening" of the surface. The silver obtained is still quite impure and must be refined by special methods usually carried out by treatment of the silver with oxidizing chemicals in crucibles.

CHAPTER XV

THE METALLURGICAL TREATMENT OF ZINC SCRAP

Apart from zinc scrap, representing the chief source of supply in the production of secondary zinc, a small amount of zinc is derived from residues and wastes produced by the metallurgical and electro-chemical industries. Metallurgical wastes of this type are practically limited to retort scrap and converter dust produced in the smelting of zinc and lead ores. In view of the chemical and metallurgical nature of these products, which are chiefly composed of the oxides or sulphides of zinc, the extraction of the metallic values cannot be effected by ordinary metallurgical methods.

Retort wastes consist of the remainder of the original retort materials, together with varying proportions of zinc ore, unconsumed coke, and coal, as well as a certain amount of metallic zinc. This material which represents a large part of the dumps of old smelters in Europe and America, differs somewhat from the retort wastes of modern smelting plants consisting of unsmelted ore residues and unburned coal and coke only, the retort scrap proper being evaluated in the production of new retorts. Of the various processes of separation recommended and applied, electrical processes alone seem to be applicable in the majority of instances, the composition of the retort wastes varying considerably and requiring skillful modification of several processes to suit the particular chemical and metallurgical peculiarities of the materials treated. One of the most satisfactory processes of this type is the Huff process, which is based on the different electrical conductivities of dry zinc blende, galena, and pyrites.

Of the various electro-chemical zinc wastes, the zinc dross, zinc-lead alloy, and the skimmings produced in the galvanizing industry are of chief importance. The skimmings, consisting chiefly of a mixture of zinc oxide, zinc chloride, and ammonium chloride, and representing the major portion of galvanizer wastes, can only be treated by chemical and leaching processes, of course, and will be

considered together with the zinc ashes obtained in the production of remelted and quality zinc (page 221). The small quantities of metallic zinc globules usually contained in the skimmings are separated from the dried and powdered material by screening.

The zinc dross produced in galvanizing processes is formed by the absorption of iron by the hot zinc and collects at the bottom of galvanizing vats. If this material is subjected to the standard remelting process in the twin pot system, a large part of the original dross is regained in the form of a comparatively pure zinc, while the concentrated iron-zinc alloy obtained is subjected to distillation.

Zinc-lead alloy is only produced when impure spelter is being used for the galvanizing process. A comparatively large quantity of zinc contained in zinc-base alloy scrap such as die-casting material is recovered by distillation.

While in view of the rather liberal specifications for ordinary grades of remelted zinc, exceptional care and complicated processes are not required for its production, attention to the smallest details and careful application of special refining methods are absolutely necessary if the remelted zinc primarily obtained is to be converted into quality zinc.

Ordinary remelted zinc should not contain less than 96.5 per cent zinc with an iron and copper content of not more than 0.30 per cent each. The remaining impurities should consist of lead and tin exclusively. Quality zinc, on the other hand, should contain at least 98 per cent of zinc, with a maximum iron content of 0.15 per cent and not more than .10 per cent each of tin, copper, nickel, and aluminum. The amount of lead present should not exceed 1.2 per cent.

If the quality of the scrap zinc used for the manufacture of remelted zinc represents a fair average of the available scrap supplies, and if the process of remelting is carried out with due attention to the rules laid down in this chapter, the above figures are easily attained, while for the production of quality zinc a fair proportion of practically new and clean zinc clippings must be used, together with carefully selected and prepared old scrap material. Remelted zinc may be produced in reverberatory and in melting pot furnaces, although the former melting device is gradually being abandoned in favor of the latter, the comparatively unimportant and by no means certain advantages of the reverberatory furnace process being more than neutralized by the considerably higher initial costs and running expenses as well as by a number of serious technical disadvantages.

Comparison of Reverberatory and Melting Pot Methods.—The chief advantage usually claimed for the reverberatory furnace method of remelting zinc is the fact that in contrast to the melting pot processes, the hot zinc does not come in direct contact with iron walls, thus eliminating wear of furnace material and contamination of the zinc with iron. This contention is disproved by actual conditions however. It is true, of course, that in the reverberatory furnace the hot zinc does not touch any iron forming part of the furnace. However, while in the first place, the solubility of the iron or steel walls of melting pots may be considerably decreased by using pots made of suitable composition, by washing the inside of the pots with certain protective preparations, and by employing correct operating methods, melting in the reverberatory furnace does not necessarily imply elimination of iron, since all zinc sheet scrap, or any other kind of zinc scrap, is contaminated more or less with iron particles, which offer a much larger surface to the corrosive action of the zinc than the walls of the melting pots, and which, for this reason, will doubtlessly give up more iron to the zinc.

Advocates of the reverberatory process of zinc remelting point to the fact that the lead separating out at the bottom of the furnace is collected at the coolest section of the metallic bath. This is doubtlessly true in principle, and in this respect the reverberatory furnace is superior to the single pot system, where the comparatively high heat concentrated in the lower portion of the metal, combined with the continual disturbance of the metallic bath by charging and refining operations, counteracts to some degree the perfect separation of zinc and lead. But this difficulty is practically overcome by the twin pot system where the bulk of the separatable lead settles out in the first pot, while the rest of the free lead separates out in the second unit of the set.

Construction and Composition of Melting Pots.—Zinc remelting pots should be made considerably deeper than ordinary melting pots in order to assist in the separation of lead. While the depth of ordinary white metal pots averages about 6 to 8 inches more than the length of the radius at the rim, that of remelted zinc pots should exceed the length of the radius by at least 12 to 16 inches. With bottom-cooled zinc pots, the depth should be still further increased since in this case the heating surface is restricted to the side walls only. It may be pointed out here that air-cooling the bottom of the pots offers the additional advantage of permitting a tapping device

to be affixed to the bottom of the pot through which the lead, or lead-zinc alloy, accumulated on the cooled bottom may be tapped at regular intervals.

In view of the corrosive influence of hot remelted zinc on iron, this material is gradually being abandoned for use in zinc melting pots. Where iron is still being used for this purpose, the walls and the bottom of the pots should be made at least 1 in. thicker than is customary with white metal pots.

Really satisfactory results are only obtained with steel or semi-steel melting pots, since a high grade composition of these materials will successfully withstand the corrosive action of zinc and the refining agents used as well as that of the firing gases. The chemical resistance of steel pot mixtures may be further improved by adding a few per cent of manganese and chromium.

Protective Washings.—It is generally known that even with most favorable working condition, the longevity of zinc melting pots is limited, and many suggestions have been offered to reduce the corrosive action of the hot zinc by preventing direct contact between the pots and the charges. Most impractical of those suggestions is that advising the lining of the pots with refractory substances, such as clay or fire-clay materials. It is self-evident, of course, that in view of the mechanical treatment of the bath, such as stirring, steaming, and sulphurizing, no lining would be able to outlast one or two charges, while the valuable zinc ashes produced would always be contaminated with the lining material.

The corrosive influence of the zinc and the sulphur gases introduced into the metal in refining is decidedly lowered by washing the inside walls of the pots with milk of lime at regular intervals. A particularly effective wash is produced by grinding a mixture of equal parts of lime and graphite together, and applying a medium thick emulsion of this material with a heavy paint brush. The wash should be applied as thin as possible, since any excess would induce spalling of the dried layer, exposing, of course, the surface of the pot. It is understood that previous to each wash, the walls of the pots have to be carefully cleaned by diligent application of a strong steel brush. The use of graphite alone does not tend to give as satisfactory results, while in a mixture with lime, large flaked graphite is most satisfactory.

Single vs. Twin Pot Systems.—The great majority of zinc remelting and refining plants employ single melting pot systems for

the treatment of the zinc scrap ordinarily obtained. It will be shown, however, that in view of the various conflicting requirements of this process, or group of processes, satisfactory results cannot be obtained unless the different phases of the melting and refining process are carried out in two separate melting pots connected by a spout or trough, permitting the remelted zinc in the first pot to flow into the second, lower member of the system.

It is well known, of course, that correct melting and pouring temperatures of scrap zinc and remelted or refined zinc respectively differ considerably, although the actual melting temperatures are greatly influenced by the nature of the scrap material treated and the methods of operation employed. The larger the amount of tar and other organic materials contaminating the zinc scrap and the more careless the melting of this material, the higher the temperatures evolved. In any case, however, the melting temperatures will always be considerably higher than the pouring temperatures.

There can be no doubt that if in the single-pot method of remelting scrap zinc operations are carried out systematically, temperatures will to a certain extent be regulated automatically since, in contrast to the reverberatory furnace method, where the excessive heat absorbed by and radiated from the walls and roof of the melting units prevents appreciable variations of temperature, the metal temperatures in melting pots are easily influenced either way by intelligent organization of working methods. Excessively high metal temperatures may be caused by the combustion of the tar and other organic substances adhering to the surface of the scrap. The heavier and cleaner the scrap, therefore, the lower the degree of excess heat evolved. Thus, while a melting temperature of about 550° C. (1000–1050° Fahr.) may advantageously be maintained during the first part of the melting period, this temperature should be reduced to around 475° C. (900–925° Fahr.) shortly previous to pouring by adding a suitable quantity of heavy and comparatively clean scrap. In pouring zinc, only a small portion of the total amount of zinc contained in the pot, that is, about 500 to 600 pounds, is ladled out at a time, the lower portion of the bath being maintained as undisturbed as possible in order to avoid stirring up the lead accumulated at the bottom of the pots.

A number of zinc-remelting plants employing the single-pot method of remelting scrap zinc have introduced a modification of this process calculated to reduce the lead contents of the remelted

zinc to a practical minimum. Instead of the small type of melting pots generally employed for this purpose very large units, holding from 8 to 15 tons of zinc are used which are completely filled by the day-shift and left to stand over night at comparatively low temperatures. This causes a very large percentage of the lead to separate out on the bottom of the pot, the zinc ladled out the next morning representing a comparatively pure grade of material. It is obvious, of course, that in order to obtain satisfactory results only one-third of the total contents of the pots should be ladled out each time.

In order to remove part of the other impurities of common zinc scrap, such as tin, copper, and iron, the metal should be sulphurized and steamed after filling the pot, and the temperature of the metal reduced to about 850° Fahr. as rapidly as possible to prevent excessive absorption of iron from the melting pot during the night.

Best results are obtained if the process is carried through in the twin pot system, where the difference between melting and pouring temperatures is attained simply enough by maintaining the temperature of the second pot, used for refining and pouring, at lower temperatures than the first pot of the system in which the scrap zinc is melted down.

A very important feature of the twin pot melting plant is its pronounced suitability for the production of quality zinc, that is to say, for the refining treatment—sulphurizing and steaming of remelted zinc. While in operating a single pot system steaming and boiling with sulphur will constantly stir up the lead and cause its reabsorption by the hot zinc, the main quantity of lead settling out

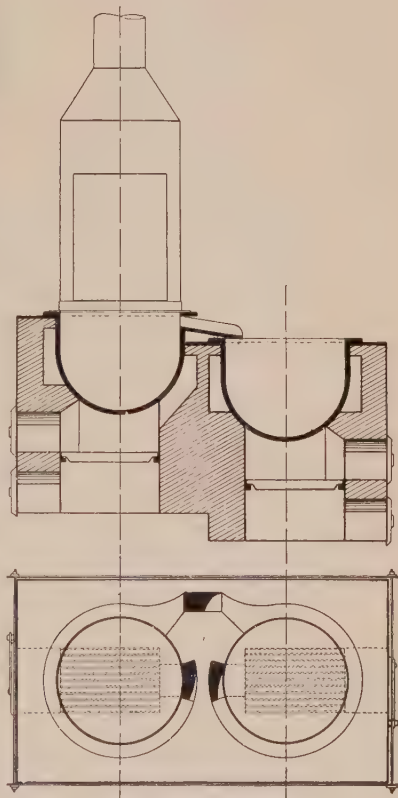


FIG. 40.

FIGS. 39 AND 40.—REMELTING ZINC PLANT.

in the first pot of a twin pot system is not disturbed by these operations. On account of the relatively small amounts of lead separating out in the second pot and the comparatively low temperatures, the refining treatment of the zinc bath does not influence separation nearly as seriously, so that a few minutes after the end of the refining treatment all separable lead will have settled out again and pouring may be commenced. Figures 39 and 40 shows the arrangement of a twin pot system for melting and refining zinc scrap.

Melting Pot Hoods and Flues.—One of the advantages often claimed for reverberatory furnaces in contrast to melting pot plants is the comparative freedom of the surrounding atmosphere from the disagreeable vapors evolved by the combustion and vaporization of the tar and other organic substances adhering to the scrap. However, the smoke nuisance does not represent an inherent disadvantage of the melting pot process. If the hoods of the pots are made large enough to take care of the large amounts of smoke and vapor produced, and if the drawing capacities and diameters of the flues are increased to suit the special circumstances, the smoke nuisance in melting pot plants is by no means greater than in the reverberatory shops.

Production of Common Remelted Zinc.—Old zinc sheets or wire should not be charged into empty pots. The melting process should be commenced by remelting a number of zinc slabs or enough heavy scrap to form a bath about eight inches deep, when thin walled scrap or wire may be charged.

The more tar and other organic impurities present the lower should be the working temperatures of the process. Normal melting temperatures, 950 to 1000° Fahr., are best recognized in practical work by the dark red glow emitted by the free surface of the zinc bath if the hood is almost closed.

Zinc scrap strongly contaminated with tar should not be charged into the melting pot since the heat of combustion generated by the burning tar will invariably cause the oxidation of most of the zinc material contained. If such material in an uncleaned condition is accepted by the smelter at all, it should first be subjected to a preparatory cleaning treatment by placing it on inclined iron plates heated from below, thus melting off most of the tar present.

The ashes accumulating on the surface of the metal must be taken off whenever a thickness of about $\frac{1}{2}$ inch has been reached. Besides

rendering the charging of fresh material more difficult, heavy layers of ashes will retain large quantities of metallic zinc.

Although in common remelting practice the zinc ashes are often treated with ammonium chloride before being taken off in order to remove all the metallic zinc contained, this should not be permitted, since the value of the ashes for many chemical and industrial purposes and, therefore, their market value, are considerably decreased by the presence of the chlorides introduced. The only satisfactory method of removing the granulated zinc spattered throughout the ashes is to pass the ashes over mechanical shaking sieves, producing good commercial zinc ashes, while the zinc globules are returned to the melting pots.

If the remelted zinc process is carried out in a single pot plant, removal of the ashes terminates the first part of the process and the period of agitation, which prevents satisfactory settling of the bulk of the lead present in the metallic bath. It is necessary, therefore, to allow for a short period of rest in order to assure of satisfactory separation of the various constituents. As a rule, 10 minutes suffice for this purpose. If the temperature of the bath is still too high to warrant good results, some remelted zinc slabs should be added to reduce the temperature to about 900° Fahr.

In order to take care of the gradually increasing quantities of lead or lead-zinc alloy accumulated in the pot, this should be completely emptied twice a week. The lower portion of the charge containing the lead is ladled out and reserved until sufficient of this material has accumulated to make a full charge. It is then melted in a special pot on Saturday afternoon and left to stand at low heat over Sunday, when the charge will have separated into two clearly defined layers, the upper one of which may be used in regular remelted zinc work while the lower layer, the lead-zinc mixture, is either dezincified in a reverberatory or distillation furnace, or used in the production of other alloys. However, since the lead-zinc alloys obtained are bound to contain iron and tin as well as other minor constituents, their application for alloying purposes is very limited, and since their market price is not, for this reason, very high, most smelters producing considerable quantities of remelted zinc should operate at least one zinc distillation unit to separate the zinc. The resulting lead-tin alloy, the iron contents of which are easily removed, represent valuable and useful raw materials, of course.

The process of removing some lead from the initial lead-zinc alloys obtained in the remelting of scrap zinc can be much improved by employing melting pots supplied with bottom taps. The material is left to stand quietly until the temperature has dropped sufficiently to cause solidification of the upper zinc layer. The lower portion made up of the zinc-lead-tin alloy, possessing a much lower freezing point, is then tapped.

Figure 10 illustrates a cross-section of the type of melting pot best suited for this purpose, although on account of the special working conditions characteristic of the zinc-remelting process, the stopper device shown interferes with the charging and refining operations. Satisfactory results are obtained by closing the outlet with clay plugs secured by a steel plate fastened to the protruding rim of the outlet channel.

The method of remelting zinc scrap or secondary zinc slabs in the twin pot plant is obvious. The raw material is charged into the first pot of the system, which is slightly raised above the second. The partially de-leaded zinc flows over into the second pot. It is self-evident that a high degree of separation of lead from zinc can only be achieved if, as explained above, only a comparatively small quantity of zinc is ladled out at a time, leaving the lower portion of the bath undisturbed.

Once a week, the second pot is ladled out until the operator reaches the level of the lead-zinc alloy, which is easily recognized by experienced smelter hands by its greater sluggishness. This alloy is then ladled over into the first pot, from which the upper layer of comparatively pure zinc has also been removed. The accumulated lead-zinc alloy is permitted to remain at rest at comparatively low temperatures until the next morning, to cause the excess zinc to settle out on top. The upper layer is then ladled into the second pot and the concentrated lead-zinc alloy is cast in molds and placed in store until enough of this material has been collected to permit of a final separation.

Production of Quality Zinc.—As a rule, the purer grades of this material are produced from new and bright zinc sheet clippings and other new zinc scrap free of soldering seams, but economical considerations render it advisable to use as large a percentage of the cheaper zinc scrap grades as possible. Thus it becomes necessary to refine the remelted zinc material in such a way as to remove considerable percentages of tin, copper, and iron, a process most econ-

omically carried out by sulphurizing and steaming the metallic bath. By this treatment it is possible to remove practically all the copper, to reduce the iron contents to at least 0.07 per cent, and to remove a large proportion of the tin present, although it is practically impossible by this method to separate all the tin contained in the zinc. If considerable percentages of tin have to be removed, it becomes necessary, therefore, to refine the remelted and partially purified zinc by distillation or electrolytic processes.

It should prove to be a very simple matter for most melting works, however, to reduce the tin contents of their remelted and quality zinc by carefully selecting and preparing the scrap material previous to charging, a large percentage of the total amount of tin present in the remelted material being derived from the soldering seams carried by a large part of the zinc scrap treated.

Very little can be said at present regarding the comparative efficiency of the various methods now used for the removal of soldering seams, none of which may be considered sufficiently developed to give entirely satisfactory results. The different mechanical cutting apparatus suggested for this purpose can only be used economically for the treatment of sheets and, perhaps, troughs, while for zinc containers, such as bathing tubs, zinc boxes, etc., the oxy-acetylene burner or a sort of electric boring-cutting tool may be employed. The latter apparatus closely resembles the ordinary boring apparatus, differing from this in the peculiar development of the boring tool which in this case acts as cutting mechanism. If the oxy-acetylene torch is used, a strongly reducing flame must be maintained, of course. The slight amount of zinc oxide vapor evolved as well as the whitish coloration of the edges of the cut need not be seriously considered.

Removal of Iron, Copper and Tin.—The iron contents of remelted zinc are derived from two sources: the original iron contained in the scrap treated, and the iron absorbed from the iron material mixed with the zinc scrap as well as from the walls of the melting pots.

Since practically every kind and grade of zinc scrap is bound to contain a certain amount of zinc-plated iron material, contamination of the remelted zinc with iron from this source has to be accepted as an unalterable fact. It is practically impossible technically and economically to guard against the presence of iron scrap. Absorption of iron from the melting pots may be reduced to a minimum by carefully paying attention to the preventive measures outlined above,

that is to say, by employing steel pots of good composition, washing the walls of the pots with milk of lime or lime-graphite emulsions, and maintaining sufficiently low working temperatures. If these rules are conscientiously followed, the iron contents of remelted zinc may be maintained as low as 0.10 per cent without further refining, provided the scrap zinc used did not contain too much iron, and if the melting-down process has been carried out sufficiently careful to preclude the absorption of appreciable quantities of iron from the iron materials contained in the scrap.

An excess of iron may be reduced to from 0.08 to 0.06 per cent by a sulphurizing treatment. It is impossible, however, to eliminate all the iron present in remelted zinc by any melting pot method, while the minimum figures above given are attainable only if the sulphurizing treatment is carried out with gasified sulphur, that is to say, if the sulphur sticks are immersed in the molten zinc by means of perforated iron boxes. The sulphur vapors formed rise through the melt, stirring the metal up vigorously and causing intimate contact of the gaseous sulphur with all parts of the metal. Apart from the bulk of the iron removed by this process, most of the copper contained will be eliminated, although it is decidedly more difficult to sulphurize the copper out of its combination with zinc than from its solution in lead. Since it is a well known fact that all copper cannot be sulphurized, it is evident that, all assertions to the contrary notwithstanding, it cannot be eliminated quantitatively from remelted zinc. A small quantity of tin is also sulphurized by this process.

The small amount of sulphur dissolved in the zinc bath after sulphurizing the metal, and a considerable percentage of the tin present in remelted zinc may be removed by steaming. The use of boiler steam should not be considered for this purpose. In view of the comparatively long and thin pipelines connecting the pot with a boiler steam system, condensed water may easily be formed, even with superheated steam plants. On entering the hot zinc this may cause dangerous explosions. A very efficient and absolutely safe steaming device, well suited for this purpose is described on page 134.

As a rule, about 10 minutes of steaming will remove the last traces of sulphur and cause the elimination of an appreciable proportion of the tin present. Since a comparatively large amount of zinc is also oxidized, excessive steaming will prove unprofitable. If steaming and sulphurizing is carried out simultaneously, the former

should be kept up about 5 minutes longer than the latter in order to remove all traces of sulphur.

After sulphurizing, the zinc bath will sometimes develop a slightly yellowish coloration which is seldom removed by subsequent steaming. The reason for this peculiar phenomenon has not been definitely determined, but it appears that this coloration will usually appear if electrolytically bronzed cast zinc has been added to the charge. At any rate, the constituents which may be responsible for this reaction are present in so small amounts as to defy detection by chemical or microscopical analysis.

If steaming does not remove the coloration, addition of about 100 grams of aluminum per ton of zinc treated will cause its disappearance. The small quantity of aluminum thus introduced (about 0.01 per cent) does not exert any noticeable influence on the chemical or mechanical properties of the zinc.

Treatment of Ashes.—Pure zinc ashes, that is to say, ashes free from chlorides and from most of the metallic zinc usually present in form of globules or small pieces of sheet scrap, may be sold to paint works, where they are further refined and employed in the manufacture of zinc oxide paints or to smelters which convert the oxides into spelter.

If chlorides of any kind are known to be contained in the ashes, it is advisable to remove the chlorides by leaching with hot water, the increase of market value obtained exceeding considerably the expenses of the process. Chemical refining of the zinc ashes should not be attempted unless the quantities of this residue produced warrant the costs of installing a chemical department, since the small margin of profit attainable does not permit the refining of small quantities of crude zinc ashes.

The same is true of the skimmings derived from galvanizing works, which after the removal of the metallic zinc by crushing and sieving, are subjected to the leaching process with hot water. By another method the skimmings are leached first and the semi-solid mass is dried and crushed. The metallic zinc contained is flattened out by the crushing process and is removed by screening, while the dry oxides are sold to paint works or ore smelters.

CHAPTER XVI

REMELTING ALUMINUM SCRAP AND RESIDUES

Aluminum scrap and residues differ from most other nonferrous scraps and residues in that only metallic scrap, dross, borings, etc., can be treated. The reduction of residual oxides, while technically possible, is a practical impossibility. Another characteristic of this branch of metallurgy is the fact that, apart from mechanical purification of the aluminum, extensive refining of the metal is practically impossible under residue smelter conditions. Thus, there are few chemical aspects to the entire process, which involves no other consideration than the most careful and efficient extraction of the residues and remelting of the scraps. The problems facing the metallurgist are by no means simple, however, and the percentage of metal lost by oxidation and insufficient extraction is comparatively high.

Classification of Scraps and Residues.—Aluminum scraps may roughly be divided into three different groups, (1) high grade scrap, consisting of clean and pure scrap materials containing from 98 to 99 per cent aluminum, (2) medium grade scrap, qualitatively as good as the high grade material, but containing comparatively large percentages of light and small pieces, such as small clippings, punchings, turnings, etc., (3) old aluminum scrap, covered with dirt and oxides, foundry scrap, such as runners, risers, gates, defective castings, etc., covered with foundry sand, slag, and other surface impurities, and, finally, small machining scrap, consisting of turnings, borings, etc., which is always contaminated with cutting oils, grease, etc.

The high grade scrap includes clean aluminum castings, bars, sheets, wires, large clippings, etc., made from a- or b-class virgin aluminum (98 to 99.3 per cent purity), the impurities of which consist chiefly of iron and silicon. The rich skimmings and drosses, as well as splashings and drippings produced in aluminum foundries may also be grouped under this heading, but these are almost invariably returned to the furnaces of the foundries themselves, very little of this material appearing in the open scrap market.

Aluminum residues consist mainly of skimmings, drosses, and sweepings, containing comparatively large percentages of aluminum oxide or dirt, and varying from 10 to 75 or 80 per cent aluminum.

The recoveries obtained from the various grades of scraps and residues vary with the aluminum contents, the amount of oxides, dirt, oil, and grease present, and the melting or remelting processes employed. The recovery on high grade fabricating scrap should be about 95 per cent, but may by careful operation be raised to 98 per cent, or even more. In remelting loose borings and similar scrap the average recovery ranges from 75 to 80 per cent, although briquetting this material will reduce the loss of metal by oxidation and nitridation by more than 30 per cent.

The recovery of aluminum from the average drosses and skimmings depends largely upon the amount of aluminum present, size and state of the metallic contents, nature of the preliminary treatment involved, and efficiency of the smelting operation. With material containing about 50 per cent of metallic aluminum, the recovery ranges from 50 to 70 per cent, depending upon the various factors enumerated.

Preliminary Treatment of Aluminum Scrap and Residues.—

The preliminary treatment of aluminum scrap and residues involves the removal of foreign metals present in loose form or attached to the scrap by handpicking or magnetizing, baling or briquetting small scrap in order to prevent excessive oxidation, and as perfect a separation of the metallic constituents of residues from the earthy material as possible.

Scrap consisting of aluminum castings or large pieces of fabricated scrap material are simply subjected to a careful examination. Loose pieces of other metals are picked out, while fittings, handles, studs, attached to scrap castings are removed.

Clean borings and similar scrap material are passed over a magnet, while larger pieces of copper and other non-ferrous metals are picked out by hand during magnetizing. Magnetic disc type separators appear to be giving best results. Considerable loss of aluminum by oxidation may be caused by melting borings, turnings, etc., contaminated with oil and grease, the difference in recovery between clean and oily borings amounting to as much as 20 per cent of the total amount of metallic aluminum melted. The most common method of removing the bulk of the oil present is to submit the material to temperatures of not higher than 550° Fahr., old furnaces or other

appliances heated with waste heat being used for this purpose. Washing with hot water removes but little of the oil, while centrifuging and washing with gasoline, although quite effective in principle, are too expensive methods to be applied under ordinary smelter conditions. Wet aluminum borings are dried as quickly as possible. The presence of dirt on the borings influences the efficiency of the melting process the same as oil or grease.

Earthy materials, such as dirt, cement, small pieces of refractory materials, etc., may be removed from clean, dry borings by screening.

The loss of aluminum by oxidation is considerably decreased by baling and briquetting. All light and thin-walled aluminum scrap, such as sheet clippings, wire, long turnings, etc., should be baled into compact bundles of convenient size, a standard baling size being 5 x 5 x 13 inches. The initial costs of the installation of a baling press, and the costs of operation are more than made up by the substantial saving of aluminum attained. Very small sized scrap, such as borings, washings, powder, and small turnings, should be briquetted into compact bricks. The size of the bricks ranges from 2 x 2 x 10 inches to 3 x 3 x 12 inches, although some European smelters prefer to handle much smaller bricks of various sizes and shapes. Aluminum foil is also added to the briquetting mixtures.

While baling of aluminum scrap reduces the loss of aluminum by oxidation by 10 to 20 per cent of the loss sustained in melting loose scrap, briquetting may decrease this loss by 30 to 35 per cent. Careful experiments carried out by Hirsch¹ showed that, under the particular experimental conditions involved, the loss of aluminum by oxidation amounted to 13.8 per cent if the scrap charge consisted of loose borings, while after briquetting, the total loss was 8.1 per cent. This advantage is accompanied by a considerable reduction of the time required to melt the scrap. Loose borings required about 50 minutes, while the briquetted material was completely melted within 30 minutes.

It is self-evident, of course, that while briquetting borings and similar material will appreciably decrease the oxidizing influence of the air, it cannot do away with the oxide already present on the scrap. In view of the fact that this kind of scrap material, as available in the open market, contains a considerable percentage of oxide, the melt produced is bound to be contaminated with comparatively large amounts of aluminum oxide, varying from 7.5 to 10 per cent.

¹ E. F. Hirsch, *Elektrochemische Zeitschrift*, 1914, pp. 1092-1094.

This percentage is still further increased if dirty and oily machining scrap is contained in the briquettes, while the total loss of aluminum by oxidation suffered in melting down briquettes is much lower if clean and bright borings only are used.

In some instances, binding materials are added to the briquetting mixtures. While these are of little use in improving the densities of the bricks, which if made in sufficiently powerful presses is little short of that of pig metal, they may become valuable if possessing a pronounced fluxing action on the oxide contents of the aluminum bath.

Principles Governing the Remelting of Aluminum Scrap and Residues.—The specific properties of aluminum which influence the success of the remelting process and the choice of furnaces and refractory materials are:

1. The strong affinity of aluminum for oxygen and nitrogen, and the influence of the oxygen contents of aluminum on the nitridation of this metal.

2. The low specific weight of aluminum which prevents the separation of the oxides and numerous other solid and semi-solid impurities by differing specific gravities.

3. The difficulty of coalescing small globules of melted aluminum separated by coatings of aluminum oxide, oil, and dirt.

4. The corrosive influence of aluminum on iron and the refractories commonly used.

The strong affinity of aluminum for oxygen does not lead to serious oxidation of the metal below a certain critical temperature usually considered to range from 900 to 1000° Fahr. The surface of the metal becomes covered with a thin film of oxide which practically prevents further oxidation unless the aluminum is present in form of very small particles, when oxidation will proceed more or less rapidly, depending upon the other factors of influence, until the aluminum is converted entirely to aluminum oxide. Very thin aluminum foil or aluminum powder in a state of fine division, if ignited, will burn with great violence, while borings or other similar scrap material will rapidly be converted into oxide at ordinary temperatures if continually subjected to the influence of moisture.

Thus, it appears that the rate of oxidation of aluminum depends upon the following factors: (1) temperature, (2) size and shape of pieces, that is, the relation of exposed surface area to weight or volume of the pieces, (3) oxygen contents and temperature of the

atmosphere to which the metal is exposed in the solid or liquid state, (4) state of dryness of the scrap, and nature of impurities coating it, (5) time of exposure.

The question of solubility of aluminum oxide in metallic aluminum is not definitely settled, but modern scientific research appears to disprove any solubility at ordinary temperatures. The melting point of aluminum oxide (Al_2O_3) is 3670° Fahr.

In melting aluminum under ordinary melting conditions, such as obtaining in aluminum smelters, oxidation of liquid aluminum does not become serious at temperatures below about 1400° Fahr. Moderate overheating above that temperature will do no appreciable damage if the metallic bath is permitted to stand quietly, since the skin of oxide formed separates the metal quite effectively from the oxidizing influence of the atmosphere. The large amount of oxides produced in remelting small sized or thin walled aluminum scrap in spite of careful operation is not caused by oxidation of the fused metal but is introduced by the skins of oxide adhering to the scrap, while excessive additional oxidation is only caused by faulty charging of scrap and careless treatment of the bath. Superheated aluminum should not be agitated, but must be permitted to cool off as quickly as possible by introducing carefully some heavy pieces of high grade, clean scrap.

The affinity of liquid aluminum for nitrogen also is of considerable practical importance. Although, according to Tschischewski,¹ nitridation of aluminum commences at a temperature of about 750° Fahr., it is of comparatively small practical importance at temperatures below 1300 to 1400° Fahr. The presence of aluminum nitride in aluminum drosses is easily detected by a strong smell of ammonium hydrate evolved if the hot dross is moistened with water. While earlier authorities believed that the nitrogen contents of liquid aluminum are due to the absorption of the whole of atmospheric air, it is now well known, that nitrogen is also absorbed if liquid aluminum is subjected to the influence of nitrogen alone.

There can be no doubt, however, that the affinity of liquid aluminum for nitrogen is considerably increased by the presence of large amounts of oxide in the metallic bath. The absorptive capacity of aluminum for nitrogen is also promoted by the presence of carbon, iron, and chlorides, a factor of particular significance if the aluminum is melted in iron melting pots and if the common aluminum flux,

¹ Journal Iron and Steel Institute, Vol. 92 (1915) pp. 47-97.

zinc chloride, is employed in the removal of aluminum oxide from aluminum baths.

Apart from oxygen and nitrogen, liquid aluminum at higher temperatures tends also to dissolve hydrocarbons which, similarly to nitrogen, may be detected by moistening the hot drosses, a decided smell of acetylene indicating the presence of hydrocarbons. It is an undisputed fact that the presence of considerable amounts of aluminum nitride in liquid aluminum promotes its absorptive capacity for hydrocarbons, so that if nitrogen is found in aluminum, hydrocarbons are almost certain to be present also, unless the construction or type of melting furnaces employed precludes the entrance of the products of combustion into the melting chamber.

Prevention of Oxidation.—It is evident from the above that the prevention of excessive oxidation of aluminum will also be instrumental in decreasing considerably the rate of absorption of nitrogen and hydrocarbons.

Opinions concerning the most effective means of preventing oxidation vary considerably. While European authorities do not consider the presence of protective fluxes an effective protection against oxidation, much more weight being placed on the maintenance of an unbroken oxide skin on the surface of the metallic bath and on perfect furnace design and correct working methods, most American authorities appear to agree on the necessity of covering the bath with protective fluxes which, besides isolating the metallic surface from the oxidizing influence of the atmosphere, dissolve the oxides introduced into the metal by the scrap.

Some of the other preventive measures, such as baling and briquetting the scrap, have been discussed above.

Nature and Action of Aluminum Fluxes.—The various fluxes employed in melting and remelting aluminum may be divided into three main groups, although in a number of cases certain fluxes may be considered as belonging to several of the groups indicated:

1. Mechanical fluxes which, without direct chemical action on the constituents of the metallic bath or the atmosphere, prevent oxidation of aluminum by forming a liquid layer impervious to the air.

2. Chemically active fluxes which dissolve the oxides introduced by the scrap as well as the dirt coating of small particles, which, together with the oxide films, prevent coalescence of the small globules of metal.

3. Volatile fluxes which are converted into vapor at ordinary

melting temperatures and cause separation of oxides and dross mainly by mechanical action.

It has been mentioned before that in contrast to American authorities, European metallurgists are not convinced of the protective action of fluxes, which are mainly used to remove the oxides and the dross directly previous to pouring. In an article, laying down their experiences and opinions, Walter Rosenhain and S. L. Archbutt, two well known British authorities, correctly express this viewpoint by the introductory paragraph quoted below:¹

“The strong chemical affinity of aluminum for oxygen and the consequent rapid formation of oxide when unprotected aluminum or alloys rich in aluminum are exposed to contact with air at high temperatures, suggests at first sight that the use of protective coverings and particularly of fluxes would be eminently desirable if not essential in the melting of these materials. In practice, this is not found to be the case and a large proportion of industrial melting of aluminum and its light alloys is carried out without the aid of protective coating whatever. The reason for this practice is not far to seek; it resides in the fact that the oxide skin which is formed on aluminum or alloys rich in aluminum is very tough and appears to be largely impervious to oxygen, with the result, that, once formed, it only thickens slowly and serves as an excellent protection to the metal below. It has been suggested that this oxide coating, which consists probably of Al_2O_3 , is capable of reacting with molten aluminum in contact with it, forming a suboxide which is soluble in and diffuses through the aluminum, which it is supposed to damage. In itself this suggestion does not appear very probable in view of the fact that a lower oxide of aluminum is not known to chemists. Further, recent researches on the behaviour of aluminum which has been repeatedly remelted and thus exposed for a prolonged period to the possibility of such an action, have shown conclusively that the material is not damaged by such a proceeding. There is also some evidence to indicate that no oxide of aluminum is at all readily soluble in the molten metal and that the formation of oxides both in aluminum and in aluminum-rich alloys is confined essentially to the surface, whether the material be in the liquid or the solid condition.”—and further on:

“The use of reducing fluxes (protective) has certain disadvantages and serious difficulties. These are due in the first place to the difficulty of preventing contamination of the molten aluminum by enelo-

¹ The Metal Industry, London, 1924, pp. 419-421.

sure of particles of flux. This difficulty arises from the fact that the density of the molten metal itself is not very much greater than that of the molten flux and, consequently, if globules of molten flux become entangled in the metal they do not separate very quickly and are liable to be carried forward into the casting when the metal is poured from the crucible or ladle. This disadvantage is so serious that in many cases it renders the use of flux undesirable. Where the use of flux is unavoidable, as for instance in the electrolytic preparation of the metal itself, it is generally desirable to remelt the metal after a first casting, in order to allow entangled particles of flux to rise to the surface and become separated."

The logic of these deductions cannot be denied, but it is impossible in practical melting operations to maintain an unbroken oxide skin on the metallic bath. For instance, if a normal piece of aluminum scrap is charged into a half filled crucible exhibiting a well developed oxide skin, most of the skin is removed in the first place, which, unlike liquid slag, will not return to the surface except in form of dross. Whatever skin remains on the surface of the metal will be removed by the tongs holding the piece of scrap and slowly moving it to and fro below the surface until melted. Thus, it appears that the question of protective fluxes cannot be solved in a universal way, but is subjected to the various conditions obtaining in each and every foundry or smelter. However, when light scrap, such as turnings and borings, are being melted, a suitable flux appears to be required, since it is practically impossible to sufficiently protect the surfaces of very small pieces against oxidation in any other way. Furthermore, it is necessary to choose a chemically active flux, which dissolves the oxide skins already present on the scrap and induces coalescence of the small globules of molten metal.

Suitable fluxes for melting aluminum scrap should answer the following requirements:

1. They should be able to dissolve aluminum oxide, silicates, and dirt.
2. Their specific gravity in the molten state, alone or if carrying dissolved oxides and impurities, should be lower than that of liquid aluminum, although in melting borings and similar scrap the difference should not be too pronounced in order to prevent immediate separation of the flux from the coated aluminum particles.
3. They must not be deliquescent.

4. Their melting point should range from 900 to 1200° Fahr.
5. Their corrosive action on the crucible and furnace refractories should not be excessive.
6. They should be reasonably cheap.

Of the chemically active fluxes, the halogen compounds of alkaline metals are universally applied. As a rule, these fluxes consist of mixtures of the chlorides and fluorides of sodium and potassium, the fluorides representing the most important members of the mixtures. In melting borings, turnings, and similar small-sized aluminum scrap, mixtures of sodium chloride and calcium fluoride are also used. The action of these flux-mixtures is mainly to dissolve aluminum oxide, while a certain small amount of gases formed by partial decomposition of the salts will dissolve silica and dirt. Where comparatively low melting points of fluxes are desired, some lithium chloride and potassium chloride is added. Best results are always obtained, of course, if the melting point of the flux-mixture is lower than that of aluminum.

While the alkali-halogen fluxes represent permanent fluxes, added to provide protective covers during the entire melting process, and frequently mixed with small scrap, such as borings, before charging, the second group of fluxes, the so-called volatile fluxes, are added at the end of the melting period immediately previous to pouring. The action of these fluxes is chiefly mechanical, the upward currents of metal produced by the vapors generated causing the impurities to rise to the surface of the bath. A certain chemical reaction is also exerted, however, by the chlorine liberated, which attacks silica, aluminum oxide, and most of the dirt carried into the metallic bath by the scrap.

Of the two compounds used for this purpose, zinc chloride and ammonium chloride, the former is doubtlessly the most valuable, since apart from its powerful action on the various impurities present, it causes the formation of a dry and easily handled dross.

The chemical action of all these fluxes is not restricted to the charges alone, of course, the iron or steel containers, in the melting pot treatment, as well as the crucible materials and other refractories used being subject to pronounced mechanical and chemical corrosion. By entering into the pores and cavities of the refractories, the fluxes and slags dissolve the bonding materials and wash away the insoluble particles, while the chemical action of these substances is directed

towards the solution and slagging of the silica and silicon present in the refractories.

The third type of fluxes, the refining or oxidizing fluxes, are quite frequently employed in Europe but do not appear to find much favor with American smelters. Most of the commercial remelted aluminum is, as a rule, sold without further refining treatment, and for ordinary purposes, as, for instance, the production of castings which do not require exceptional mechanical qualities, and the properties of which are not closely defined, the ordinary remelted aluminum suffices.

There are many industrial requirements, however, which offer additional possibilities for the sale of the refined material. In drawing and rolling aluminum, for instance, the finished products, made from ordinary remelted aluminum, will be perceptibly harder than wire and plates or sheets manufactured from virgin aluminum; it will also show more or less blistered surfaces. In refining aluminum by means of oxidizing fluxes, a certain additional loss of aluminum by oxidation and dressing will be incurred, of course, but this is amply compensated for by the higher prices paid for the purer material.

For refining aluminum, only such oxidizing substances should be used which—with rapid and intelligent application—will not cause appreciable contamination of the aluminum, or more than ordinary wear of furnace materials. Particularly useful for this purpose have been the bichromates of potassium, sodium, and ammonium, or mixtures of these, as well as the nitrates, permanganates, and chlorates of several metals, and a number of other, less frequently used chemicals which, upon being heated to temperatures of from 1100 to 1250° Fahr., will yield free oxygen. Potassium nitrate, sodium nitrate, and ammonium nitrate should not be used, however, since in decomposing these substances will yield potassium, sodium, and ammonium, which contaminate the product, spoiling its mechanical properties.

The refining treatment applied is simple. About 2 to 3 ounces of the flux per 100 pounds of aluminum are wrapped in a moist piece of blotting paper and pushed down to the bottom of the crucible or hearth, so that the molten and vaporized decomposition products are forced to rise up through the entire charge, oxidizing the impurities, together with a comparatively small amount of aluminum. The refining of aluminum by this method should take place directly after melting down the scrap, and should be followed by the ordinary

purification treatment with zinc chloride, which will remove all traces of the refining substances used.

Very little chromium or other metallic components of the refining or oxidizing fluxes are absorbed by the aluminum if working conditions are right, and it has actually been shown that these do not hurt the quality of the aluminum, but tend to improve its mechanical properties. Other refining processes, not involving chemicals, will be discussed later.

Types of Furnaces Used for Melting Aluminum Scrap and Pig.

—The following types of furnaces are used for melting and remelting aluminum scrap and pigs:

1. Crucible furnaces,
2. Iron and Steel melting pots,
3. Reverberatory furnaces,
4. Electric furnaces.

In view of the high degree of affinity of aluminum at high temperatures for oxygen, nitrogen, and hydrocarbons, the metal must be protected as much as possible against the action of atmospheric air and the products of combustion. Such furnaces are to be preferred, therefore, that prevent the contact of the molten aluminum with air and gases, or, at least, allow of the most perfect regulation of gas compositions. Although electric furnaces serve this purpose best, a number of other important factors enter into the problem, which may render the use of other furnaces more expedient.

Crucible Furnaces.—In view of the comparatively small quantities of aluminum scrap and remelted pig usually treated in the average smelters or foundries, iron-melting pots and crucible furnaces are still most largely employed, the former being generally preferred in America, while European metallurgists tend to favor the latter.

As a rule, graphite crucibles are used for this purpose. Since the melting products of the process, and the fluxes used, possess a pronounced affinity for silica, the silicious components of the crucible mixtures are rapidly dissolved from the walls of the crucibles, which gradually become brittle under the influence of heat. To overcome this difficulty, lining the graphite crucibles with a thin layer of clay has been attempted, but this practice has been discontinued by most works, the inferior heat conducting properties of such crucibles caus-

ing a decided prolongation of the process and a correspondingly higher loss of aluminum by oxidation.

The size of the crucibles used for this purpose has been continually increased, until to-day the largest types have reached capacities of 500 pounds and more. The advantages of large sized crucibles are:

1. The larger the weight of each charge, the more rapid the rate of melting of a given amount of scrap, and the lower the relative fuel consumption.

2. Larger sized pieces of scrap may be charged without causing comparatively high losses of metal by falling over the walls of the crucible.

3. Large crucibles are not removed from the furnace for pouring, thus eliminating excessive breakage caused by regularly recurring abrupt changes of temperature and by careless handling. The reheating of the cooled crucibles is also avoided, saving fuel and time.

The general properties and treatment of graphite crucibles are discussed in detail in a special chapter on "Melting Crucibles."¹

Good crucibles should contain at least 60 per cent of graphite and possess a very low degree of porosity. Apart from permitting the penetration of the gases of combustion into the metal, porous crucibles will take up moisture at every opportunity, causing the formation of cracks and fissures. The size of the graphite flakes used in the crucible mixtures should be as large as possible, the strength of the crucibles and their resistance against softening depending upon the amount of graphite present and upon the size of the flakes. Slag forming substances such as soda, potash, lime, and the oxides of iron and manganese should not exceed 2.5 per cent, the amount of the alkalis present remaining below 0.4 per cent. The crucible mass must be free from organic impurities which, when decomposed by the heat are bound to cause spalling and the formation of cracks.

The crucible furnaces generally used for melting and re-melting aluminum are not essentially different from the types of furnaces used for the production of bronzes and other non-ferrous metals and alloys. These may be divided into coke, gas, and oil fired, stationary and tilting crucible furnaces, with or without forced draft, of which the tilting pit coke furnace is the one most commonly used in smaller

¹ Melting Crucibles, pp. 289.

foundries. Besides greatly facilitating operations, tilting furnaces permit of a considerable saving of crucible material and heat, since the crucibles need not be lifted out of the furnaces at each pouring. Larger sized crucibles can only be employed in conjunction with tilting crucible furnaces, of course.

In order to avoid the several disadvantages connected with the use of the stationary type of pit furnaces, as, for instance, insufficient control of heat, danger of contaminating the aluminum with coke dust and ashes, etc., the author has successfully applied the ordinary iron-melting pot furnace type to the melting of aluminum. The graphite crucible is placed into the space ordinarily reserved for the melting pots, but not directly above the grates. The fire gases are thus made to rotate around the lower half of the crucible, and are then drawn upwards into a flue channel encircling its upper portion. The rim of the crucible extends about half-an-inch above the top of the furnace. This method of construction of the crucible furnace is particularly adapted to large crucibles, while for reasons above expounded, small crucibles should be used with tilting furnaces.

The Crucible Process.—After placing the crucible into the furnace, a small quantity of hot coke is placed into the pit and covered with some dry and small sized coke. Moist and large sized pieces of coke should not be charged. Large sized coke prevents the free descent of fresh coke, thus interrupting the melting process and causing the formation of an ash rich in unburned coke particles, while moist coke causes a relatively high loss of heat energy and tends to damage the crucible walls by penetration of the hot steam formed.

Before charging the metal, the crucible is heated to redness, that is, to a temperature sufficiently high to cause rapid liquefaction of the first 50 to 100 pounds of metal charged. The metal should not be allowed to drop down into the empty crucible but should be charged by means of tongs. Care must be exercised in any case to prevent scratching and scraping of the crucible walls by the sharp edges and corners of the scrap. Excessively large pieces must be cut up or broken, not only to prevent damaging the crucible, but also to enable the material to be pushed below the surface of the liquid metal as quickly as possible, preventing undue oxidation of the large surfaces. It is a generally recognized fact that in remelting aluminum scrap more metal is oxidized while the solid material is being melted than after it has reached the molten state and has been able to accumulate

a protecting skin of oxide. The crucible should never be filled completely with solid scrap, which becomes red hot a long time before melting and accumulates a heavy layer of oxide. A few heavy pieces should first be added, which when fused form the bath in which all the other metal is gradually immersed.

The comparatively high resistance of red hot aluminum to melting, in spite of the elevated temperatures obtaining within the crucible, is due to the high specific heat and the high latent heat of fusion of this metal. The specific heat of aluminum at 100° Centigrade amounts to 0.232, as against 0.093, 0.03, and 0.113 in the case of copper, lead, and iron respectively, while the latent heat of fusion is 263 Calories (Cal/Kg). It is thus necessary, in spite of the comparatively low melting point of aluminum, to supply a larger amount of heat than would be required to melt copper. This fact possesses the marked advantage that the molten material may be kept fluid much longer than most other metals and alloys.

Fusibility and Melting Points of Metals.—It is a common error among foundrymen to regard the fusibility of metals and alloys as being more or less synonymous with the respective melting points.

The melting points of metals indicate the temperature at which the solid materials pass into the liquid state, without, however, specifying, or even indicating, the quantitative values of the melting reaction.

The fusibility of a metal or alloy is governed by the latent heat of fusion, or the amount of heat—in Calories—necessary to convert one kilogram of the metal from the solid state into the liquid state.

Table 37 shows the important technical metals arranged in the order of their melting points.

TABLE 37

1. Tin.....	232° C.	450° F.
2. Cadmium.....	321° C.	610° F.
3. Lead.....	327° C.	621° F.
4. Zinc.....	419° C.	786° F.
5. Antimony.....	630° C.	1166° F.
6. Magnesium.....	650° C.	1202° F.
7. Aluminum.....	658° C.	1216° F.
8. Silver.....	961° C.	1762° F.
9. Gold.....	1063° C.	1945° F.
10. Copper.....	1083° C.	1981° F.
11. Nickel.....	1450° C.	2642° F.
12. Platinum.....	1764° C.	3207° F.

Table 38 shows the same metals arranged in the order of their respective degrees of fusibility and their latent heats, expressed in Cal/Kg.

TABLE 38

	Fusibility, cal. per kg.	Latent heat, cal. per kg.
1. Lead.....	17.0	4.0
2. Tin.....	27.0	13.8
3. Cadmium.....	32.0	13.1
4. Gold.....	52.0	16.3
5. Zinc.....	68.0	22.6
6. Antimony.....	74.0	40.2
7. Silver.....	87.0	24.4
8. Platinum.....	91.0	27.2
9. Copper.....	153.0	43.0
10. Nickel.....	188.0	68.0
11. Magnesium.....	220.0	
12. Aluminum.....	263.0	100.0

Thus it is seen, that while—for instance—the melting point of gold is 400° C. higher than that of aluminum, the quantity of heat necessary to melt one kilogram of aluminum would suffice to melt 5 kilograms of gold.

After enough metal has been charged into the crucible to form a primary bath—about one third of the total capacity—the furnace is filled with coke up to the edge of the crucible. While charging the coke, the crucible should always be covered with a lid to prevent impurities from getting into the metal. As soon as the first scrap charge has melted down and assumed a bright red color, fresh scrap is charged and melted, if possible, by holding it below the surface of the metal to diminish the rate of oxidation. If the metal begins to show signs of cooling, charging is stopped and the metal brought back to red heat. Remelting is continued until the crucible is filled up to about 4 inches from the top, when directly previous to pouring, the metal is subjected to a refining treatment.

If impure, dirty, or oily scrap is being treated, intermediate refining and skimming may be in order—as a rule, whenever the layer of dross on the surface of the metal has reached a thickness of about 2 inches.

The practice of charging adopted in each and every case varies, of course, with the nature and condition of the scrap treated. It is self-evident, that all aluminum scrap must be charged in a perfectly

dry state and that wherever the material has not been stored in a warm and dry place for a sufficiently long time previous to charging, it should be subjected to a temperature of at least 225 to 250° Fahr. Very often, the scrap is dried by piling it up on top or around the furnaces.

Heavy and thickwalled pieces of scrap are held into the metallic bath until dissolved. Light scrap or loosely baled material are rarely brought down into the bath, but are placed on the metallic surface and left to melt down without stirring up the metal. If such material forms the bulk or the whole of a charge, a bath, or "heel," of metal is usually prepared by melting down about 30 per cent (of the total amount of the charge) of pig metal. The contents of the crucible are not interfered with until this is filled up to near the brim, although if throughout the melting process the layer of ashes reaches a thickness of about 2 inches, it is removed in order to facilitate the fusion of the scrap. Unbaled sheet and wire scrap should only be melted by immersion into the bath, although the loss of metal by oxidation will be very high in any case, especially in treating unclean or corroded material.

The melting temperatures should at no time exceed a maximum of 1350° Fahr. Temporary super-heating, which may be caused by short interruptions in charging is neutralized by charging a few heavy pieces of scrap, which are moved to and fro as quietly as possible to avoid undue disturbances of the surface. Stirring should under all circumstances be avoided while the metal is in an overheated condition.

The maximum temperature indicated refers to melting operations in the crucible furnace only. If aluminum is melted down in a strictly neutral or reducing atmosphere, such as prevails in electric furnaces, a certain limited degree of overheating is actually of advantage, since on account of the corresponding decrease of the viscosity of the melt, mechanical impurities are more easily separated out on the surface of the bath, while, on the other hand, larger percentages of metallic aluminum liquate out from the dross.

Melting Aluminum Drosses.—While protective fluxes are not always used in melting or remelting scrap, it cannot be dispensed with in treating aluminum drosses. There can be no doubt that these drosses submit to economical smelting only if subjected to proper preliminary treatment and smelted with suitable fluxes. The preliminary treatment consists of crushing the dross in hammer crushers

and removing the bulk of the oxides or semi-oxides contained by screening.

The success of the crushing treatment of drosses depends upon the type of crushers employed. Good results are only obtained if the action of the crusher is of a crumbling or jarring nature, separating, as it does, the oxides and non-metallic constituents of the drosses and skimmings without pressing or kneading a large proportion into the metal. Hammer crushers or ball mills are best suited for this purpose, although the suitability of the various types and makes of the disintegrating apparatus is not always the same with different types of drosses and skimmings.

Before charging the metallic concentrates of the crushed drosses, it is necessary to provide for a sufficiently deep bath of molten and hot aluminum. The concentrates are then added in small lots, together with a small amount of a mixture of about 85 per cent of cryolite and 15 per cent of salt (sodium chloride). The dross is taken off twice with each heat. This is crushed and sieved, and the metallic concentrates are recharged. Before pouring the crucible, the aluminum is treated with zinc chloride to remove the oxides and other impurities suspended in the metal. A short refining treatment may also be given if deemed necessary.

Melting Light Scrap.—Particular attention must be paid to the treatment of light scrap, such as filings, borings, chips, etc., although from a practical point of view this is more simple than that of the average drosses. Where this type of scrap consists of clean and dry material, the simplest and most efficient method is to stir the scrap into a sufficiently preheated bath of aluminum, covered by a thin layer of protective flux. It is good policy to produce the original layer from virgin aluminum, and several important smelters prefer to use about 30 per cent of virgin aluminum whenever remelting light and thin-walled aluminum scrap.

The crucible should never be filled with fine material while empty, but should first be charged with heavy scrap or ingots enough to fill about one-third of its total capacity. After this has been brought to red heat, a shovelful of the fine material is added, and stirred into the bath. After a while, the charging is stopped and the bath, which has cooled down almost to the melting point of aluminum, is brought back to red heat again, and so on.

Too large an amount of ashes should not be permitted to collect on the surface of the metal, since this will prevent sufficiently rapid

immersion of the light aluminum scrap into the bath. It is necessary, therefore, to skim the ashes or dross whenever the layer has reached a thickness of about 1 or 1½ inch.

Another method of treating the light aluminum scrap is to keep the bath in a semi-melted condition until the crucible is practically filled. The bottom of the crucible is covered with a layer of about 3 or 4 inches of molten aluminum, by melting down a few heavy pieces of scrap or a few ingots of virgin metal. One or two shovels full of light material are then charged and stirred until the entire mass is in a semi-melted condition. New material is then added and similarly treated, and the process repeated until the crucible has been filled. Care must be exercised throughout the entire process not to soften the mass more than necessary to agglomerate the charge. The crucible is finally covered with a tightly fitting lid, and the aluminum "paste" brought to a complete melt, which is subsequently cleansed by one or several of the fluxes indicated. With first quality, clean and dry aluminum chips and burnings, an average yield of about 80 to 85 per cent of metal may thus be obtained, while old turnings more or less oxidized by exposure to moisture, etc., will yield as low as 30 to 60 per cent of metal.

Still better yields may be obtained by mixing the borings and similar scrap material with about 25 per cent its own weight of a mixture of 80 per cent of sodium chloride and 20 per cent of powdered fluorspar. This mixture is charged and heated, and as soon as softening commences the material is tamped down and fresh material added. This process is repeated until the crucible is nearly filled. Heating is then continued until all has been sufficiently liquefied, the slag is removed, and the metal poured. By this method a maximum yield of 95 per cent is often attained with first-class material, while the purity of the product is also considerably higher than that obtained by the other methods.

The best method of melting aluminum borings, turnings, chips, and other light aluminum scrap under ordinary foundry and smelter conditions has, in the author's experience, been the one first described, that is to say, the stirring of the fine material into a bath of metal.

Before pouring, the surface of the aluminum, as well as the rim and the projecting inside walls of the crucible must be thoroughly cleaned. If compressed air is available, this should be used to blow off ashes and dust; if not, a pair of strong bellows will give good service. If hand ladles are used, these must also be freed from dust

and, eventually, rust deposits. If large slabs of metal are to be poured, no fire-clay-lined ladles should be used, but graphite pouring crucibles.

If the melting of aluminum scrap has been carried out with due care, the success of the pouring process is almost exclusively governed, directly or indirectly, by the pouring temperatures employed, which may range from 1350 to 1475° Fahr. according to the size and shape of the castings. The ill effects possibly due to temporary superheating of the melt may be eliminated to a large extent by correct pouring temperatures, as is shown by the results of the following three experiments, carried out with an aluminum alloy composed of 85% aluminum, 3% copper, and 12% zinc.

The first sample was heated until zinc vapors commenced to make their appearance; the melt was then cooled down to normal temperatures by the addition of cold scrap, the temperature again raised to 1650° Fahr., and the metal poured at a temperature of 1250° Fahr. The test bar produced showed an ultimate tensile strength of 13.2 kg/sq. mm. and an elongation of 0.5%.

A second sample melt was heated to 1650° Fahr., deoxidized, and poured at 1475° Fahr. The ultimate tensile strength of this test piece was found to be only 10 kg/sq. mm., while similar results were obtained with a test bar obtained from a melt produced, deoxidized, and poured at 1550° Fahr.

Different conditions obtain if metallic aluminum is overheated considerably for a prolonged period of time, and it is practically impossible in this case to obtain good mechanical properties. Due to the strong absorptive capacity of aluminum for nitrogen and the hydrocarbons at elevated temperatures, these gases must be eliminated before pouring, a process most successfully carried out under practical working conditions by cooling the melt down to its freezing point, bringing it back to correct pouring temperatures as carefully as possible.

The strength of aluminum is greatly influenced by the length of time required to convert the liquid metal into a solid. The more rapid the cooling process, the stronger the casting. Thus, the lower the pouring temperatures, the less heat is given off to the mold material and the shorter the cooling period influencing the strength of the casting. Heavy and thickwalled castings may be cast at a temperature of as low as 1250° Fahr.

This fact explains the well known experience that aluminum test

bars cast with the castings in one piece will exhibit mechanical properties quite different from those of the casting proper, unless the strength of the test bar corresponds to that of the casting. Test bars cast in one piece with thin-walled castings will always exhibit lower tensile strength than the casting, while with increasing thickness of the casting this difference is gradually reversed.

“Refining” Aluminum.—Apart from the use of oxidizing salts or fluxes, as described above, a very satisfactory degree of refining may be attained by leaving the molten bath standing quietly for from 10 to 24 hours, while if this method appears to be too tedious, similarly good results are claimed to be obtained by letting the bath cool down gradually below its freezing point, and bringing it back to pouring temperatures very slowly. There can be no doubt, of course, that the latter method is more or less efficient in freeing the aluminum from dissolved gases, but it is hard to see what influence it should have on the removal of the various common impurities of aluminum which are suspended in the bath because the similarity of specific weights prevents them from rising to the top.

A third physical method of refining aluminum is to raise the metal to a temperature of about 1650° Fahr., holding it for one or two hours, then cooling it off to normal temperatures, a method to be adopted only if the aluminum is remelted in crucibles or electric furnaces. The advantages claimed for this method are:

1. On account of the diminished viscosity of the metal at the increased temperatures, separation is facilitated of all those impurities, the specific gravities of which are but slightly higher than that of aluminum.

2. While the quantities of oxides formed are not, of course, diminished, there is a decided lowering of the amount of dross formed, since its metallic contents are enabled to liquefy out, leaving almost dry oxides on the surface of the metal. The fact that by superheating the metal, particularly after being remelted a number of times, a decided deterioration of its mechanical properties is often experienced, does not prove the impracticability of this method. It is not the high temperatures of the metal, but the absorption of gaseous impurities, particularly nitrogen and carbon monoxide, which is responsible for the lowering of the mechanical properties. If satisfactory provisions are made for the protection of the metal against the absorption of the constituents of the products of combustion, and with correct working manipulations, no trouble will be experienced

from this source. Superheating aluminum in reverberatory furnaces is, for this reason, not advisable.

Remelting Aluminum in Iron-Pots.—The melting pot furnace, while serving its purpose well enough for treating aluminum alloys, does not appear to be as satisfactory a melting device as graphite crucibles or any of the other melting appliances generally used for remelting aluminum scrap and residues, particularly if no efforts are made to adapt the iron materials composing the melting pots to the peculiarities of the process. The deficiency of the iron-pot furnace for this purpose is exclusively due to the lack of resistance of practically all iron compositions to the corrosive action of the aluminum at the comparatively high temperatures of the process, although the influence of these temperatures alone would doubtlessly suffice to break down the resistance of the iron-pots under the purely mechanical strains implied by the melting process. While in the production of all types of white metals or in remelting lead, tin, or other metals possessing a comparatively low melting point, iron or steel pots represent the most satisfactory type of melting appliance, their usefulness is decidedly less pronounced whenever the treatment of these metals requires appreciably higher temperatures as, for instance, in refining lead. It must be assumed, therefore, that in remelting aluminum scrap in iron-pots, the high temperatures involved play an important part in the rapid destruction of the pots and that, in consequence, an iron mixture calculated to resist higher temperatures would also exhibit better resistance qualities under the conditions of the aluminum melting process.

The failure of iron pots in this work may be due to the following reasons:

1. Chemical corrosion by the molten aluminum.
2. Mechanical erosion following preliminary corrosive action.
3. Chemical corrosion by the various fluxes used.
4. Cracking, spalling, and scaling, due partly to the corrosive and erosive actions of the metal and fluxes, and to the considerable fluctuation of temperatures.
5. Scaling of the outside of the pots due to the corrosive action of the flames and to the intensity and the fluctuations of temperatures.
6. Action of comparatively dry drosses or ashes containing finely divided metallic aluminum which, if subject to strong oxidizing in-

fluences, such as the presence of oxidizing fluxes incline towards spontaneous combustion, generating temperatures sufficiently high to cause fusion of the iron with which the burning particles of aluminum happen to be in direct contact.

Corrosive Action of Aluminum on Iron at High Temperatures.—

It is practically impossible to prevent solution or corrosion of iron at high temperatures by any fused metal with which it may remain in permanent contact. In melting lead, tin, zinc, aluminum or any of the white metal alloys in iron or steel-melting pots, in zinc—or tin-plating iron materials, in working any kind of metallic baths with iron or steel tools, in pouring metals by means of iron ladles, and such like, iron is dissolved and, consequently, will contaminate the non-ferrous metals involved. The influence of the fused metals or alloys and the iron upon one another, which is due only to their capacity of forming solid solutions with each other, is quite different under the various conditions of temperature, dissimilar physical condition of the iron, etc. Of all the white metals in question, aluminum may be considered to possess the most corrosive action on iron.

Very little reliable data have been made available as to the resistance of various iron and steel compositions against the corrosive influences of hot molten aluminum and the various fluxes involved, but the comprehensive experiments carried out by R. Irmann¹ have shed considerable light on the influence of the different components of cast iron on the wearing qualities of iron-pots.

It has been generally known for some time that low carbon steels and iron are not nearly as resistant to the action of fused aluminum as gray cast irons, and the experiments of Irmann showed that while iron containing from 0.1 to 0.2 per cent of carbon yielded about 3 per cent of iron to liquid aluminum (time of exposure, 60 minutes), the loss of iron by a sample containing 1.5 per cent carbon proved to be less than 0.5 per cent, the percentages named representing the amount of iron contained in the aluminum after a one-hour exposure at temperatures of about 1650° Fahr. Diffusion of aluminum into iron, or, in other words, absorption of iron by aluminum diminished with increasing percentages of carbon, proving, that, apart from the direct or indirect influence of graphite, the combined carbon possesses a strong influence on the resistance of gray iron to absorption by aluminum.

¹ Zeitschrift fuer Metallkunde, 1925, p. 273, and 1926, pp. 64–68.

Silicon, which in gray iron is present in amount of from 3 to 4 per cent, also exerts an appreciable influence on the resistance of iron to the action of liquid aluminum, chiefly because in decomposing the iron carbide it increases the graphite contents of the iron. Irmann's results show that an increase of 3 per cent silicon in a 1 per cent silicon iron reduces the amount of iron absorbed by aluminum under the conditions of the experiment from about 2.7 to 1.5 per cent.

It is to be expected that in view of these facts, gray cast iron represents a much more desirable material than steel, and it has been shown that under exactly similar conditions, aluminum will dissolve practically 13 times as much iron from steel pots than from gray iron containers.

The corrosive influence of liquid aluminum is greatly influenced by the surface condition of the iron. Gray iron covered with a heavy skin of iron oxide, especially the natural pouring skin of cast iron, is much more resistant against molten aluminum than iron unprotected by such a layer. The protective influence of the natural skin is due in part to the presence of small particles of sand and slag in the skin, which prevent "wetting" by the aluminum, although by far the greatest influence in this direction appears to be exerted by the Fe_4O_3 in the skin, produced by the action of air on the fresh metallic surface of the iron. If, for instance, one of two new testing crucibles cut from a heavy iron rod is strongly oxidized previous to filling with aluminum and heating, it will be found that the oxidized crucible is considerably more resistant to the action of aluminum than the other. This difference is still more pronounced in the case of steel, where the amount of iron absorbed from the unprotected crucible may be three times as large as that lost by the oxidized container. This fact may be evaluated, of course, by increasing the protective influence of the skin of cast iron melting pots by artificial oxidation, such as is used for rust proofing, etc.

The absorption of iron by aluminum is also appreciably decreased whenever the iron surface is covered by a burned-in skin of aluminum. For instance by emptying an aluminum melting crucible or pot and heating it, while empty, with only a skin of aluminum adhering to the walls, the pots will be much more resistant to the corrosive action of liquid aluminum than untreated pots. In the case of steel pots, the amount of corrosion, as measured by the iron contents of the aluminum charge of a pot, is reduced by 50 to 60 per cent.

In using melting pots for remelting aluminum scrap, attention

must therefore be paid to the composition of the pot material and to the surface conditions of the pots. One of the best iron compositions for the manufacture of these pots is the following:

	<i>Per cent</i>
Total Carbon	3.5
Combined Carbon	0.4
Manganese	0.8
Sulphur—Max.	0.15
Phosphorus—Max.	0.5
Silicon	2.25

To increase the resistance of the pots to the oxidizing influence of the firing gases as well as to the internal strains caused by the thermal fluctuations, a chromium content of about 2 per cent will be useful. The natural skin of the iron pots should under no condition be injured, as is very often done in order to improve the general looks of the castings.

A number of foundry equipment manufacturers are now offering aluminum melting pots of special compositions, and several of these products have been found to give satisfactory service under normal foundry and melting conditions. Figures 41 and 42 represent an aluminum melting pot made by the Aluminum Foundry Equipment Company which is offered in sizes of from 9¼ in. to 15½ in. depth and from 15½ to 19½ in. inside diameter.

Aluminum spout pots used in connection with tilting aluminum furnaces are shown in Figures 43 and 44.

In order to prolong the life of melting pots, washes or castings are often applied, although it appears rather doubtful, whether any of the various methods suggested are of much practical use. In choosing between the effectiveness of coatings or washes, if the former term applies to comparatively heavy layers of resistant materials, and the latter is used to designate thin protective, skin-like applications, washes are doubtlessly the most desirable, since heavy coatings, no matter how ingeniously composed and carefully applied, cannot be made to adhere firmly to the walls of the pot. In charging any kind of scrap, and in working the metallic bath, patches of the coatings are bound to come loose, contaminating the metal, and opening a breach through which the hot liquid aluminum will immediately commence to wash away the rest of the protective layers. The application of these coatings to aluminum ladles must be viewed from

a different angle, since apart from the absence of serious mechanical strains, the coating serves as insulating agent, preventing the formation of heavy skulls of metal. The refractory materials most commonly used for this purpose are fire-clay and magnesia cement.

Comparatively fair results may be obtained with the applica-

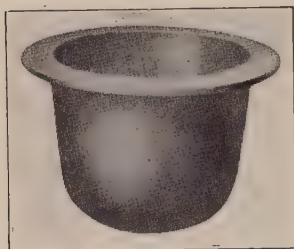


FIG. 41.

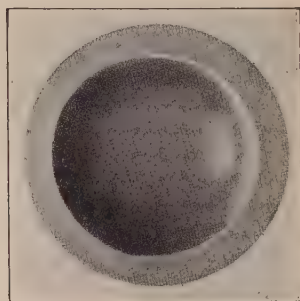


FIG. 42.

FIGS. 41 AND 42.—ALUMINUM MELTING POT.

tion of suitable washings, provided these are made to adhere to the walls of the pots and renewed as frequently as possible.

One of the washes most generally used in Germany consists of a mixture of graphite and lime ground together and made up to the



FIG. 43.



FIG. 44.

FIGS. 43 AND 44.—ALUMINUM MELTING SPOUT POT.

consistency of a thin paste with water. Before applying the wash, the walls are carefully scraped off and all metallic particles adhering to the pot removed. The paste is then applied with steel brushes, thus forcing the particles of graphite and lime into all the surface cavities

and fissures of the walls. The pot is then heated to a temperature of about 1100 to 1250° Fahr. for about 1 hour before charging is commenced.

Other washings are composed of lime and fire-clay mixtures, and similar materials, but these do not adhere as well as the graphite-lime mixture mentioned.

An apparently very efficient surface treatment is based upon the fact above indicated that a thin layer of burned-in aluminum on an oxidized iron surface possesses a distinct protective action against the influence of molten aluminum. This has been made use of in an English patent (146,841, 1919). According to this patent the inter-

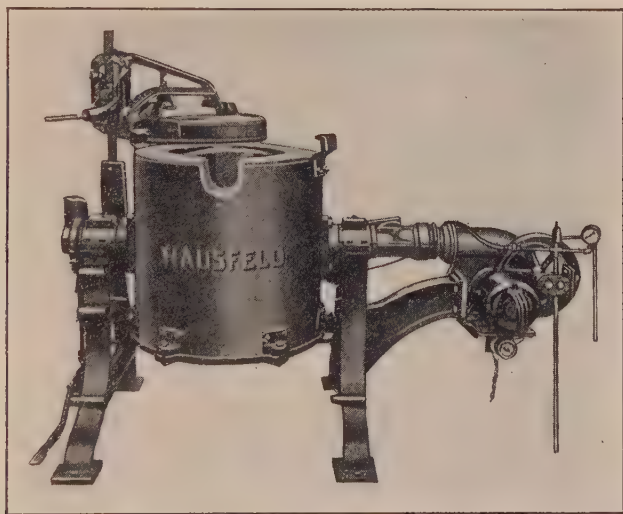


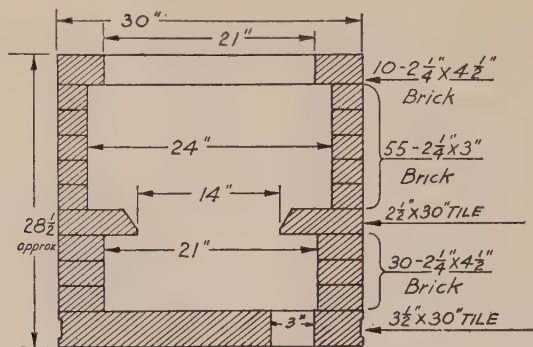
FIG. 45.—TILTING TYPE MELTING FURNACE.

nal walls of the pots are coated with a thin layer of an aluminum varnish, which is "burned-in" by heating the pots slowly to a temperature of about 400° Fahr.

While for the production of ingot metal the ordinary melting pot furnaces used in secondary metal melting works give perfectly satisfactory service, tilting furnaces may often prove necessary, especially if aluminum or aluminum alloy castings are to be produced. Figure 45 represents a Hausfeld Tilting type aluminum melting furnace using a cast iron pot of a capacity of 300 pounds of metal per heat.

This furnace may be heated with natural or artificial gas, oil, or

kerosene. Figure 46 shows the arrangement of the lining, and the combustion chamber of this furnace.



—13—

FIG. 46.—LINING AND COMBUSTION CHAMBER OF TILTING TYPE MELTING FURNACE.

Melting Aluminum in Iron Pots.—While in view of the widespread use of iron-pot furnaces it appears inconsistent or one-sided to insist upon the poor suitability of iron pots for this purpose, it may generally be conceded that the smelting of residues poor in aluminum should be left to other types of furnaces, such as the crucible furnaces. Melting pots give comparatively satisfactory service in remelting metallic aluminum scrap of all types, excepting, perhaps, fabricating scrap, such as turnings, borings, etc., where the relatively large amount of fluxes generally used exert too strong a corrosive influence on the iron material of the pot. It is quite certain that in spite of this outstanding disadvantage of iron pots, the better heat conducting properties of iron and the much greater mechanical strength of the pots in strenuous service give the latter a considerable advantage over graphite crucibles wherever these properties form important requirements.

The various processes used in melting and remelting aluminum do not vary in any way if carried out in iron pots, although in view of the perfect heat conducting properties of iron, the various phases of the processes are considerably shortened.

Remelting Aluminum Scrap in Reverberatory Furnaces.—Wherever regular supplies of large quantities of aluminum scrap are to be remelted, reverberatory furnaces are frequently used, furnaces of from 5 to 10 tons capacity representing the average. Reverberatory furnaces are also required where large castings are to be pro-

duced, or where, as for instance in rolling mills, etc., large quantities of aluminum of absolutely uniform purity must be available; also for the production of large quantities of aluminum alloys, and for the remelting of large supplies of loose thin-walled scrap, such as clippings, wire, a.s.o., which are pressed into comparatively large bales.

On account of the rapid oxidation of the metal in direct contact with the firing gases and of the absorption of comparatively large amounts of nitrogen and hydrocarbons from the products of combustion, reverberatory furnaces may, however, be used successfully only where the output is large and the aluminum need not remain in the furnace for too long periods at a time.

In order to eliminate these advantages as far as possible, operation of reverberatory smelting must be guided by the following principles:

1. The furnaces should be constructed so as to decrease as much as possible the relative surface area of the bath per unit volume of metal, and to provide for a tap at least 5 inches above the hearth elevation at the tap hole. In order to make provision for a complete emptying of the furnace, a slit tap about 6 inches high may be provided, although the tapping section of the furnace is made considerably stronger if two tap holes are used, the upper one for general tapping, and the lower tap hole for emptying the furnace after a series of heats of the same batch of raw material.

The advantage of maintaining a bath of metal in the furnace is obvious. It serves as a bath for the next charge, preventing excessive loss of aluminum by oxidation which, as has been shown above, is decidedly more pronounced during the melting-down period of a solid aluminum body exposed to the oxidizing influence of the air.

Figures 47 and 48 show the construction of an aluminum reverberatory furnace built in accordance with the requirements of the processes involved:

2. The loss of aluminum by oxidation and its contamination with nitrogen and hydrocarbons may be still further reduced by intelligent operation. Before filling an empty furnace, this should be superheated to about 2000° Fahr. for about 2 or 3 hours. Firing should then be reduced to a minimum and charging commenced with heavy, thick-walled pieces of scrap or with heavy pig, which are melted down by the excess heat absorbed by the bottom, walls, and roof of the furnace. As soon as a bath has formed, charging should be

continued by holding the solid material below the surface of the bath, moving it to and fro until melted.

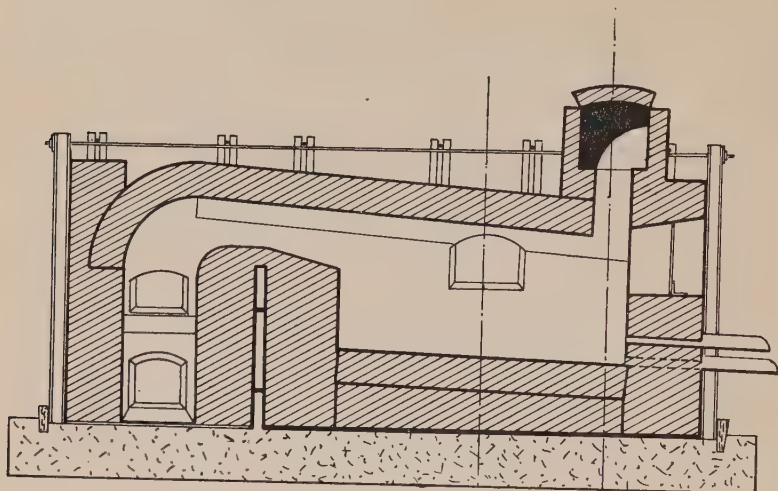


FIG. 47.

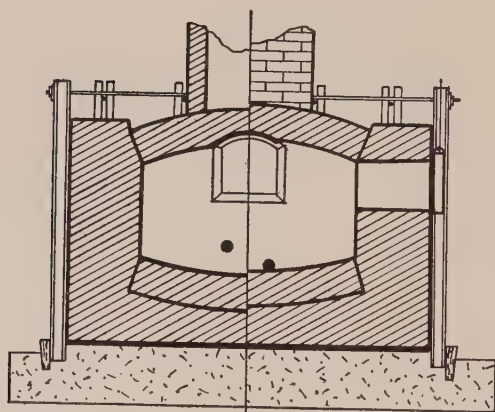


FIG. 48.

FIGS. 47 AND 48.—ALUMINUM REVERBERATORY FURNACE.

The use of protective fluxes, while considered unavoidable in many smelters, is not as general as may appear natural under the circumstances, the only flux universally applied being zinc chloride, which

is added at the end of the melting process. The metal is then left to stand quietly until cooled down to about 1350° Fahr. and tapped. The skin of aluminum oxide formed during this period is not removed until the surface of the metal has descended to a few inches above the level of the tap hole. In order to improve the purity and quality of the aluminum, the metal in reverberatory furnaces is often left to stand quietly for 12 to 15 hours, that is, over night, particularly if protective fluxes have been used in the process, which are thus permitted to settle out.

Electric Furnaces.—On account of the non-existence of organic products of combustion in electric furnaces, eliminating as it does the danger of contamination of the metal by carbohydrates and excessive quantities of nitrogen, electric furnaces possess a decided advantage over any other type of metallurgical furnace—excepting melting pots and certain types of crucible furnaces. However, their suitability for general aluminum melting purposes is considerably lessened by the comparatively high heat developed, which in the case of practically all directly or indirectly heated electric furnaces causes a comparatively large loss of metal by oxidation. Other considerations such as low heat efficiencies also constitute serious disadvantage.

Considering the various methods of applying the electrothermal effect of the current, the chief types of electric furnaces may be defined as follows:

1. Direct Arc Furnaces, in which the current traverses the bath of the metallic bath forming one of the electrodes. Intense local heating occurs where the arc is formed, and also where it leaves if a series arc is formed.

2. Indirect Arc Furnaces, in which the arc is formed between the electrodes sufficiently high above the metallic bath to heat it by radiation only. Intense local heating is thus avoided.

3. Indirect Resistance Furnaces, also known as "Resister Type Furnaces," in which the heating effect is produced by passing the electric current through an electrically resistant refractory wall, often the walls of the crucible, or through special resister carbon placed in a circular trough near the roof of the furnace, the heat generated being radiated on to the metal surface by the roof.

4. Induction Furnaces, in which the heat is generated in the metal bath without the use of electrodes, the metal itself forming a com-

plete secondary circuit in which the resistance to the alternating current effects the heating.

The direct arc furnace, due to the intense local heat generated, is absolutely unsuitable for aluminum melting purposes, and while the original furnaces of this type have been very much improved to adapt them to non-ferrous metal and alloy melting, aluminum cannot be melted in any of these furnaces without suffering excessive loss of metal by oxidation.

The indirect arc furnace, while eliminating intense local heating of the bath, differs from the direct arc type of furnace in degree only. It is obvious that on account of the white heat of the arc, the electrodes must be removed as far from the surface of the bath as possible, so that the roof of the furnace must be located sufficiently high to provide for the proper distance between the surface of the metal and the source of heat. However, since each additional square inch of wall space introduces a correspondingly larger loss of heat by radiation, and since in order to hold the oxidation losses down to economic figures the arc must be located several feet above the metal surface, the heat efficiency of the indirect arc furnaces is too low to qualify them for this purpose.

The induction furnaces used for general non-ferrous melting are not suitable for aluminum work as yet, although strong efforts are being made by the Ajax Company and their affiliated works in Europe to adapt the Induction furnace to the chemical and physical properties of aluminum. Apart from the strongly corrosive action of the rapidly flowing current of hot aluminum, oxides are settled out in the induction channel of the furnace, and while the former difficulty may of course be surmounted by introducing suitable refractory materials, the clogging up of the channel presents a rather difficult problem. It appears, however, that this problem is near its solution at the present time and that the introduction of induction furnaces for aluminum melting purposes may soon be expected.

The general advantages of the induction type of furnace over practically all other melting furnaces are obvious. Since the heat is generated within the metal itself, and since the metal is always hotter than the furnace walls and the air space above, perfect temperature control is ensured, while, for the same reason, this furnace is the most economical in regard to low power consumption and melting cost.

It takes a perfectly regular and even load without fluctuations, so that melting may be conducted perfectly to scheduled times. Since the metal represents the hottest part of the unit, loss of metal by surface oxidation is reduced to an absolute minimum.

The only basic disadvantage of the induction furnace lies in the fact that on account of the continued circulation of the metal, "refining" of secondary aluminum by segregation is impossible. However, since this kind of work is generally carried out in large capacity reverberatory furnaces, this consideration is of more or less an academic nature only.

Of all the various types of electric furnaces used at present, only the indirect resistance furnaces may be considered as giving fairly satisfactory service. The metal is contained in a crucible made of carbon and graphite mixtures but specially treated to make sure that the electric current passes through the walls of the crucible only, and not through the charge. The original principle of indirect resistance heating has been developed in this country by the Morgan Crucible Company. The side walls of the furnace are made of highly refractory material covered with insulating material to prevent excessive radiation of heat from the furnace. The body of the furnace consists of a steel cylinder packed with insulating material. The supports may either be of trunnion type for pouring the metal into ladles, or of the lip-axis type, which requires a spout not necessary in the other form. The flow of electric current is automatically controlled, thus ensuring perfect regulation of temperatures within the crucible. While comparatively high temperatures may be attained with this type of furnace, best results are obtained with metals or alloys fusing at temperatures below 900° C. (1250° Fahr.).

In view of the comparatively high latent heat of fusion of aluminum, the thermal efficiency of this type of furnace is not exceptionally high, unless the apparatus is used continuously, when the heat efficiency of the indirect resistance furnaces compares fairly well with that of fuel-fired melting units.

Considering all the commercial aluminum melting devices in general it appears that for melting smaller quantities of this metal, or its alloys, melting pot and crucible furnaces are still the most economical apparatus, while large amounts are best melted in reverberatory furnaces provided with deep hearths and fired with soft burning fuel. It is only a question of time, of course, when with the further advance

of the electric furnace industry electric melting appliances, especially the induction type of furnaces, will have been developed sufficiently high to give perfect service, but until that time little can be gained by producers in changing from the well established and absolutely fool proof coal and oil fired furnaces to insufficiently developed electrical apparatus. The success achieved with electric furnaces in other branches of the non-ferrous metal industry cannot serve as criterion in this case, of course.

CHAPTER XVII

REVERBERATORY FURNACES

Disregarding the treatment of copper and copper alloys or any other metals and alloys foreign to the range of subjects covered in this volume, reverberatory furnaces are employed for melting, remelting, and alloying white metals, for the reduction of white metal ashes of all types, for the preliminary elimination of copper, iron, zinc, and arsenic from white metal scrap and secondary ingot metal, for remelting and refining lead, tin, and aluminum, and for a rough separation of alloys comparatively rich in tin and antimony into several products richer and poorer in tin and antimony than the original white metal. The characteristic features of the reverberatory furnaces employed for the various purposes indicated have been considered in connection with the discussion of the respective processes.

The important parts of every reverberatory furnace heated with coal or coke are:

1. The fire-box,
2. The fire-bridge,
3. The hearth,
4. The tap,
5. The working doors,
6. The roof,
7. The flue.

Reverberatory furnaces fired with oil or gas have no separate fire-places or fire-bridges, the fuel being burned in the "laboratory" or combustion chamber. Fuel dust firing is not, as a rule, employed with white metal reverberatories.

The foundation of reverberatory furnaces may be made of stone, brick, or cement concrete. The thickness of the foundation depends on the capacity of the furnace, the specific weight of the materials treated, and the nature of the ground. It is obvious that lead refining furnaces require a heavier foundation than aluminum reverberatories.

The looser the soil the thicker and wider should be the foundation. If loose soil reaches down too deep to permit of digging to bedrock or hard pan (a mixture of clay, sand, and gravel) two layers of 4 or 5 inch planks spiked crosswise together are sometimes placed at the bottom of the pit and the foundations built on this bed.

For heavy reverberatory furnaces the foundation should be at least 2 ft. thick, while if concrete is being used, a layer of fire-clay bricks should be interposed between the concrete and the bottom plate in order to prevent warping or lifting of the concrete due to excessive downward radiation of heat. The richer the concrete mixtures the lower its resistant power towards heat, very good mixtures being the 8:1 or 10:1 mixtures. Instead of sand and gravel commonly used as lean constituents, black iron blast furnace slag in various sizes should be used in reverberatory furnace foundations in order to improve their heat resistance, while a number of smelters have obtained good results with old firebrick scrap.

The size of the fire-box, that is, the grate area, depends upon the size and type of the furnace and is directly dependent on the amount of fuel to be burned within a fixed period of time to obtain the necessary furnace temperatures. It is generally assumed that with natural draft (about 2 in. water) a square foot of grate will burn about 12 pounds of high grade coal charged to the depth of 4 to 5 inches, while with forced draft of about 5 to 6 in. water twice as much coal is consumed. This coal consumption is in the first place governed by the temperatures required and is usually controlled by draft regulation. Reverberatory furnaces for low temperature work, such as aluminum furnaces, may burn from 5 to 8 pounds of high grade coal per square foot of grate per hour, while lead refining furnaces and other reverberatories operated at higher temperatures may consume as high as 15 pounds of coal per square foot of grate per hour.

The grate bars should be thin and deep to keep them cool. The air space between the bars should not be less than $\frac{1}{2}$ inch nor larger than 1 inch. In order to prevent buckling, the bars are usually provided with projections at the center. If the length of the grate exceeds 4 feet, a center transverse bearer should be added to the two end bearers. Grates longer than 5 or 6 feet should be fired from both sides, another advantage of this arrangement being the possibility of slagging and cleaning the grates in sections.

The fire-bridge, which separates the fire-box from the hearth, must be high enough to extend at least one foot above the highest point

of the layer of fuel, allowing for a 2-inch layer of clinkers beneath the fuel to preheat the air, and for a height of the ash-pit of at least 30 inches. The upper edges of the fire-bridge should be well rounded off to permit of a smooth flow of the flame over the fire-bridge and onto the hearth. The bridge should be made hollow, to provide for air or water cooling, the free space being secured by two cast-iron plates or by sufficiently large U-irons laid on edge on top of each other.

Attention is called to the fact that U-irons will prove insufficient for perfect cooling of the fire-bridges of high temperature white metal furnaces unless the width of the cooling space exceeds 10 in. Since practically all white metals at high temperatures tend to penetrate the furnace walls irrespective of thickness wherever these are not cooled by air or other cooling agents, the fire-bridge represents the most vulnerable part of the furnace in this respect. The temperatures of the air within the cooling space may reach 700° Fahr. or more, particularly throughout the upper sections formed by U-irons, and the hot molten white metal is thus able to work its way through the bridge wall and across the cooling section, making its way between the sides of the U-irons. In spite of all apparent physical laws the liquid metal then penetrates the other half of the bridge wall towards the fire-box and finally collects in the ash-pit.

Better results are obtained if the cooling space is secured by two cast iron plates, the height of which must exceed the high level of the metallic bath within the furnace. However, while the leakage of metal into the ash-pit is usually prevented, it is often found to seep through the joint between the cooling plate and the bottom plate.

Leakage of white metal into the cooling section of the bridge may be avoided entirely by air or water cooling, unless it is decided to set the hearth of the furnace in a steel or iron pan. Floating of the furnace bottom within the pan is prevented by making an opening of about 1 in. diameter in one of the two long sides of the pan approximately 10 in. above the bottom. The metal trickling from this opening is collected in a mold.

The hearths of reverberatory furnaces, such as are employed in residue smelting plants, are usually made oblong. Occasionally they are somewhat contracted towards the flue in order to prevent the formation of dead corners at the flue end. The ratio of the width to the length of the hearth is governed by the nature of the smelting operations and by the furnace temperatures required. As a general

rule, a ratio of 3:2 will be found satisfactory for smaller furnaces. The ratio of hearth area to grate area depends on the required furnace temperatures, the height of the roof above the hearth, and the kind of fuel employed. In general, a ratio of 5:1 to 7:1 may be considered suitable for high temperatures reverberatories such as lead refining and white metal ashes smelting furnaces, while aluminum melting and liquating furnaces and similar units require ratios of from 8:1 to 10:1.

The furnace bottom is usually built up of 3 layers of brick. The uppermost layer consists of high grade fire-clay bricks stood on end; the second layer, consisting of the same high grade material, is laid on edge, while the third layer consists of fairly good fire-clay refractories. The thickness of this layer decreases towards the flue end of the furnace in order to obtain the angle of inclination of the hearth required for perfect drainage of the metal.

This method of laying the lowest layer of the furnace bottom is exceedingly tedious and, if carried out sufficiently careful to provide a perfectly solid foundation for the upper layers it requires a very high degree of skill not often possessed by the average bricklayer. This part of the construction work may therefore be carried out with advantage by the following method:

After laying the side walls of the furnace to a height of about 10 in., a layer of high grade fire-clay mortar, decreasing in thickness towards the flue end of the hearth so as to obtain the required inclination and the curvature of the hearth is placed directly on the bottom plate. Small pieces of fire-clay bricks are usually distributed throughout the full length and width of this layer to increase its carrying capacity. The layer is permitted to air-dry a few days, the cracks formed are then filled up with comparatively dry mortar and the drying period prolonged another day. A number of coke fires placed around the bottom will speed up the drying process. It is then only necessary to place the first layer of bricks directly on the dried fire-clay bed.

While exceptional attention must, of course, be paid to perfect joining of the bricks throughout all sections of metallurgical furnaces, this is particularly true of the uppermost layer of the hearth and of all those sections of the walls and the fire-bridge situated below the metal and slag levels. Open joints are primarily due to badly finished surfaces and to the use of heavy layers of unsuitable mortar compositions, while faulty drying and heating operations as well as insufficient tying of the furnace will cause the formation or re-opening

of vertical points. Since practically no bricks possess perfectly smooth and even surfaces, the bricklayers should be made to grind, or rub, the surfaces of the bricks composing the uppermost layer of the hearth against each other. This method is carried out as follows: Before laying the first brick of a row, its side is ground against the corresponding side of the proposed second brick and put in its proper place. The second brick is now rubbed against the third brick, etc. It is obvious that for the same reason heavy layers of mortar must be avoided by all means. The mechanical and chemical properties of the dry mortar are not nearly as good as those of the bricks, and since the usefulness of a hearth is determined by the quality of its weakest point, the same careful attention should be paid to each individual joint. Some of the larger Continental smelters test the joints of their reverberatory bottoms by means of the knife-test, that is to say, the joints must be too close to permit the blade of a pocket knife to be inserted between two neighboring bricks.

Since under conditions generally prevailing in small residue smelting plants it is almost impossible to attain this end, or to entirely prevent re-opening of some of the joints, recourse is often had to the use of bricks of larger size for lining the hearth and the lower parts of the walls and the fire-bridge. While this expedient does not eliminate all the danger from open joints it will at least cause a decided reduction of the total number of joints exposed to chemical action, decreasing the sources of trouble in proportion.

Instead of using the mortar mixtures ordinarily used by furnace bricklayers, dilute emulsions of the proper mortar should be employed. The moistened brick is merely dipped into this emulsion and laid into its place, tapping gently with a wooden hammer to produce a tight fit with the neighboring brick.

Of the various types of refractory bricks, fire-clay bricks, which are most commonly employed for the furnaces used in white metal smelters, are most easily worked. Silica bricks are decidedly more fragile and brittle, while magnesia bricks are too hard and brittle for this purpose.

Silica brick bottoms are not employed for any of the furnaces used in white metal melting. Magnesia bricks are sometimes employed for the uppermost layer of bricks in lead refining furnaces, while for aluminum furnaces special fire-clay bricks rich in alumina should be selected to lower the rate of corrosion of hearth and walls by the molten aluminum. Since furnace temperatures are not exces-

sively high in white metal smelting, the hearths may rest on solid foundations, while occasionally, that is to say, in smelting tin residues or in refining lead, the hearth is constructed over an air vault. Occasionally, the foundation is provided with a system of cooling channels, which may also be made to serve as passage ways for the lower tie-rods. However, since modern tendencies are directed towards increased conservation of heat, cooling of the hearth is now rarely attempted, loss of metal by penetration being prevented by constructing the hearth on a steel or iron bottom plate.

The roof usually extends uninterruptedly over fire-box and hearth, its highest point being above the fire-bridge, and descends gradually towards the flue end of the furnace. The lowest point of the roof is usually flush with the upper edge of the working door located directly beneath the exit flue. The roof forms a cylindrical arch, the main axis running parallel with the long sides of the hearth. The rise of the arch is generally fixed at about 1 inch per foot of span.

Since the roof of reverberatory furnaces is not designed to carry excessive loads, it is useless to go beyond the usual thickness of 9 in. With average temperatures of reverberatories ranging from 1500 to 2250° Fahr., it is also bad policy to try to attain this end by covering the roof with a heavy layer of sand, particularly above the fire-box. It should be kept in mind that for any given temperature approaching the practical softening point of the refractory materials employed, an equilibrium is formed which in dependence upon the softening points of these materials, their relative conductivity of heat, and the outside temperatures is expressed by a certain thickness of the roof. If the actual thickness exceeds that fixed by the equilibrium, the inner surface of the roof commences to melt away until this equilibrium—or the thickness of the roof corresponding to the equilibrium—is attained. It is absolutely useless, therefore, to attempt to save heat by increasing the thickness of reverberatory furnace roofs beyond a certain limit, even if the temperatures required by the metallurgical processes involved approach the theoretical softening and melting point of the refractories used.

It is a generally known fact that roofs of almost any type of reverberatory furnace will commence to drip or “sweat” almost immediately after having been placed into service, although the apparent maximum temperatures prevailing in the furnace remain several hundred degrees below the theoretical softening point of the bricks.

It is obvious, of course, that the actual temperatures prevailing near the roof of these furnaces, particularly above the fire-box, average several hundred degrees higher than those observed near the hearth, but this fact alone does not explain the difference still remaining between the furnace temperature and the softening point of the bricks.

The chief reasons for this phenomenon are the mechanical strains and the chemical influences of foreign substances introduced into the surface structure of the bricks in service, that is to say, the action of spattered slag, metallic and chemical fumes, gases, products of combustion, as well as that of the pressure exerted on the lower part of the roof bricks by the weight of the roof itself. The action of the foreign substances enumerated is self-explanatory. Many of the oxides of the metals, especially lead and tin oxides, possess a pronounced fusing action on the silica contents of fire-clay bricks. Similarly active, or even more so, are some of the basic constituents of the slagging materials added with the residues, such as soda-ash and lime. The chemical action of these substances is particularly strong towards the mortar, and the joints of reverberatory furnace roofs are usually hollowed out to a depth of an inch or more within a comparatively short time, exposing a steadily increasing surface of the bricks to the dissolving action of the oxides and fumes.

Less generally known is the fact that the softening and melting temperatures of refractories are considerably lowered by strong pressures and heavy loads. In laying the roofs, the bricklayers make use of wooden shapes which support the arches until the furnace is placed into service. It is clear that as soon as the arches of the roof become self-supporting a certain degree of compression is exerted upon each individual brick. This is particularly the case if in laying the roof insufficient attention has been paid to the shape and condition of the bricks employed. If the shapes are such that with a fairly good fit of the lower edges of the bricks the upper edges stand ajar, the gaps being filled up with mortar, the center of the arches will, upon removal of the wooden supports, gradually be lowered until the upper edges of the bricks have approached each other as far as the resistance of the compressed mortar and the strength of the tie-rods will permit. This movement exerts an exceedingly strong pressure on the lower edges of the bricks, and the combined effect of this pressure and the chemical influence of the metallic oxides, fumes, and gases suffice to lower the softening point of the exposed sections of the bricks several

hundred degrees. Thus, it is shown that in designing high temperature reverberatory furnaces the question of cooling the roofs is not less important than that of heat economy.

The recognition of this fact has caused numerous designers of reverberatory furnaces to approach the other extreme by installing cooling systems on the roof of the furnaces, constructing double layers of bricks and passing cold air through the hollow space thus formed with the idea of making economical use of the heat thus saved in preheating the air of combustion or in supplying drying furnace and similar auxiliary units with hot air. The futility of such an arrangement has frequently been pointed out by metallurgists and engineers, since apart from the fact that these constructions tend to complicate inspection and repairs, the saving of heat by this means becomes a matter of "robbing Peter to pay Paul."

The influence of pressure on the softening point of refractories is also of importance in considering the construction of the roof relative to the side walls. It is a well-known fact that the roofs of the majority of reverberatory furnaces constructed for the treatment of metallic residues are supported on the lining which, similar to the roof, is subjected to the maximum temperatures of the furnace, while the influence of slag, oxides and vapors asserts itself to a still higher degree. The life of the furnace walls may be prolonged considerably if the roof is laid in a manner calculated to relieve the inner lining of all unnecessary stresses. Additional loading of the furnace walls with iron construction for the purpose of mounting auxiliary machinery and apparatus such as blowers, ventilators, etc., should under no circumstance be permitted. Figure 49 illustrates the correct method of supporting the arches.

The size of the cross-section of the flue-opening is determined by the grate area, the usual ratio being from 6:1 to 4:1. In order to improve the heat efficiency of the furnace and to cause even distribution of the heat along the entire width of the hearth below the flue-opening, this cross-section should not be made square, but oblong as shown in Figure 50. For instance, instead of constructing a square flue-opening 20×20 in. the flue is flattened out against the narrow front side of the furnace, making a cross-section of, say, 12×33 in. which prolongs the path of the flames through the furnace by 8 in. A still higher degree of thermal efficiency may be obtained if an inverted flue-bridge is provided by constructing a rim of bricks, 4 to 5 in. deep, around the flue-opening. This prevents the fire-gases from

being drawn directly into the flue, but forces them to descend towards the hearth.

The working doors should be made large enough to permit of comfortable charging and working of the charges, but not so large as to

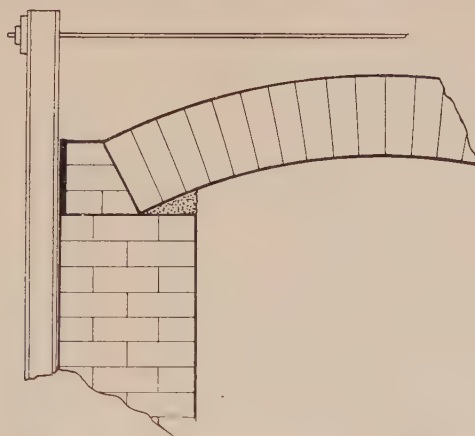


FIG. 49.—CORRECT SUPPORTING OF REVERBERATORY FURNACE ARCHES.

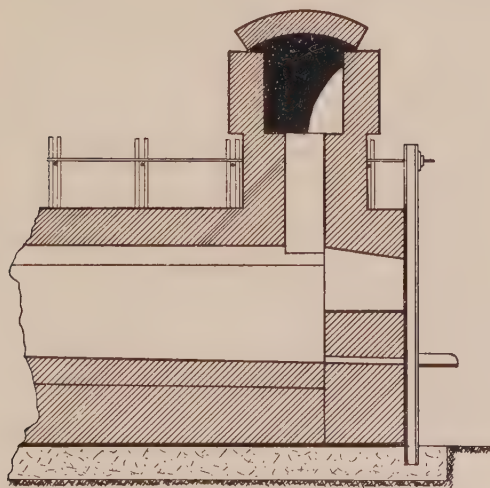


FIG. 50.—CONSTRUCTION OF FLUE OPENING.

prevent excessive cooling of the interior of the furnace. Two openings, a smaller one in one of the side walls and a larger one below the flue are usually sufficient to permit the operator to reach all sec-

tions of the hearth. The main working door should always be located below the flue opening in order to prevent excessive cooling of the furnace by the inrushing air. It is obvious that if the main opening is located in one of the side walls, the air drawn into the interior is made to traverse part of the hot furnace before reaching the flue, causing a corresponding loss of heat, while the opening of the working door directly beneath the flue opening permits the cold outside air to be drawn into the flue without entering the interior of the furnace. As a matter of fact, most small furnaces are operated from the narrow front side since this opening affords a much better view of the furnace interior, permitting the operator to reach practically every section of the hearth.

The deteriorating effect of cold outside air on the temperature of the furnace whenever the side doors are opened is largely eliminated by inserting a cast-iron damper or a fire-clay tile in the descending flue, which is kept closed if the working doors are to be opened for any considerable period. The flue should also be closed during charging in order to prevent excessive loss of metallic values by dusting. The practice of providing a few loose bricks somewhere in the brick work of the descending flue, which are removed during charging or whenever the doors are opened for any length of time, is absolutely faulty. Although the cold air drawn into the flue through these holes will materially decrease the force of the draught at the flue-opening, the draft is not entirely eliminated by any means, and the cold air thus drawn into the flue system is bound to reduce the general draft effect of the chimney.

This relative importance of the various openings is usually considered in constructing the doors, the main opening being supplied with a door calculated to combine lightness, ease of operation, and heat insulation. The doors for the auxiliary openings are made heavier in order to obtain more perfect heat insulation and heat resistance, the matter of lightness and ease of operation being of somewhat lesser importance.

It should be pointed out, however, that opinions concerning the relative importance of the amount of heat lost by radiation through the working doors are by no means uniform. Indeed, a number of authorities tend to disregard this factor entirely by suggesting the use of plain cast-iron plates instead of the massive refractory contraptions generally used. These plates are cut to loosely fit the opening and are supplied with an angle iron at the bottom to serve as support.

There are two holes in the upper part of the plate, about three inches apart, through which the prongs of a fork are inserted when lifting the plate in and out. The holes are also used to observe the temperature of the furnace. These plates have been employed successfully in a number of European smelting works for reverberatory furnaces of all types and sizes, including tin ore smelting furnaces constructed to maintain temperatures of up to 2300° Fahr. It is claimed that one of the most valuable, though least apparent, advantages of these plates is that the heat-coloration of the plate offers a rather definite indication of the approximate heat prevailing within the furnace, and the temperatures of the interior of a number of furnaces may thus be judged correctly from distances of 30 to 50 feet.

The furnace is held together by buckstays and tie-rods. The buckstays are set vertically against the sides and ends of the furnace, the lower ends being set into concrete—backed by heavy wooden blocks—while the tops are connected with the opposite buckstays by the tie-rods. The wooden blocks backing the lower ends of the buckstays serve to take up the outward thrust exerted by the expanding brick work. The method of arranging the buckstays around the furnace is determined by the length of the sides, and the location of doors, the flue, and the forehearth. Apart from the four pairs of buckstays at the corners, one pair each is usually placed at the two sides of the fire-bridge. Two pairs are also placed near the working doors—about 6 or 8 in. from either side of the opening. Other buckstays are placed at equal distances against the solid walls. The tie-rods should be placed high enough above the roof to allow for the rising of the highest arch, the longitudinal tie-rods being laid on top of the cross rods to prevent sagging.

High temperature reverberatory furnaces are usually encased in steel or cast-iron plates which distribute the pressure more evenly and serve to protect the brick work. However, these plates do not serve their purpose if they are placed against the finished walls, the protruding sections preventing the uniform contact between masonry and plate required. In constructing the furnace, buckstays and plates are put in place first and the brickwork is then laid against the plates.

CHAPTER XVIII

REFRACTORIES FOR METALLURGICAL FURNACES

While, ceramically speaking, refractory materials are such that may be subjected to a temperature of at least 2700° Fahr. without suffering deformation, this definition represents only one of the fundamental characteristics of all the refractory materials employed in furnace construction. Indeed, the various chemical and physical influences acting upon the refractories, such as the deteriorating effects of vapors, gases, slags, and fused metals, fluctuation of temperatures, pressures, etc., are of much greater immediate interest, particularly, since it is easy enough to find refractories of sufficiently high softening and melting temperatures to stand the comparatively moderate heats involved in general non-ferrous metallurgy.

In spite of the earnest endeavor of all interested industries, there is no universal refractory fulfilling all demands. It remains one of the functions of the metallurgist, therefore, to select for each individual case the refractory, or refractories, the mechanical and chemical properties of which will permit them to satisfy the most important requirements.

All refractories employed in the construction of metallurgical furnaces must—or should—possess the following properties to the highest possible degree:

1. High softening and melting points under the influence of gases, vapors, and other products of the various metallurgical processes involved, and under normal loads.

2. Sufficiently strong resistance against all fluctuations of temperature, accidental or intended, irrespective of the metallurgical processes employed.

3. Chemical and physical inertness towards the dissolving and combining influences of the fused metals and alloys, fluxes and slags, as well as towards the corrosive effects of metallic and chemical vapors produced and the gases of combustion, the high degree of influence of which is not sufficiently appreciated, as a rule.

4. Least possible change of shape and volume under practical working conditions.

5. Conductivity of heat to suit the various circumstances, that is to say, high or low, according to requirements.

6. Mechanical strength, and a high degree of resistance against blows, erosion, etc., in the hot or cold state.

7. Uniform composition and properties of refractories of equal or similar brand and designation.

8. Maximum workability of bricks in laying.

9. Accurate and uniform measurements.

10. Smooth surfaces and even, sharp edges.

11. Retention of all the above properties after prolonged periods of storing and after a sufficiently long time of actual service at maximum temperatures and under the normal conditions of the metallurgical processes involved.

Silica Bricks.—Silica bricks, as used in smelters, must be strong and ringing, edges and corners must be thoroughly vitrified and should not be subject to crumbling either in the cold state or at the normal temperatures of smelting processes and under the influence of moderate temperature fluctuations. They must be highly refractory and should not fuse at temperatures below Seger cone No. 33, the usual melting points ranging from 3100° to 3150° Fahr., thus comparing favorably with those of high-grade fireclay and bauxite bricks. The melting point of magnesite bricks exceeds that of silica bricks by about 800° Fahr., but this difference is more than made up by the higher resistance of silica bricks against temperature fluctuations.

The specific refractory superiority of silica bricks over most other refractory materials lies in the small difference between the melting points and the respective softening points under load, the latter remaining within about 150° Fahr. of the former. Fire-clay and bauxite bricks soften at 2420° Fahr., while magnesite bricks crumble at 2570° to 2770° Fahr., as against a softening point of silica of 2900° to 3100° Fahr.

In view of the comparatively high degree of expansion even of well-burned silica bricks, due allowance must be made for this property in constructing the furnaces in order to avoid excessive compressive stresses and the formation of long, wide cracks across the walls of the furnace. A silica brick containing 94.8 per cent SiO_2 and 2.1 per cent CaO , and possessing a melting point of No. 33 Seger

cone, a specific weight of 2.36, and a porosity of 23.1 per cent, exhibits a linear expansion of 1.1 per cent at 2570° Fahr. Thus, in copper refining furnaces $\frac{1}{4}$ inch of expansion space is allowed per 1 foot of roof, and $\frac{5}{16}$ inch per 2 feet of bottom.

The specific weight of silica bricks should not exceed 2.4, corresponding to a degree of transformation of 70 to 80 per cent. The coefficient of porosity of high-grade bricks should not exceed 23 per cent, since excessive porosity decreases the resistance of the bricks against abrupt fluctuations of temperatures and heavy mechanical stresses. Another disadvantage of excessive porosity is the high degree of absorption of slags and gases causing increasingly rapid disintegration of the structure of the bricks. It is a matter of practical experience, however, that the average silica brick contains approximately 27 per cent of pore space, so that a certain allowance must be made in this regard. It is self-evident that the porosity of a silica brick is more or less dependent upon the character and origin of the raw material used. Bricks produced from sharp-edged, tightly interlocking quartzite grains are bound to be less porous than others made up of rounded grains, which, apart from the higher original degree of porosity, become increasingly more porous on burning. According to Donald W. Ross,¹ the average porosity of the commercial bricks tested is 26.34; the average of the bricks made from Medina quartzite is 27.07; and the average of bricks from Baraboo quartzite is 24.30, while that of brick made from chert is 25.64.

It is almost impossible to accurately determine the quality of silica bricks by means of the tests usually applied in smelters, since the Seger cone tests do not permit conclusive deductions to be drawn concerning the practically important properties of the bricks, excepting, perhaps, the melting points, which in the case of silica bricks are quite uniform. The determination of the specific weights also will not give dependable results since it does not consider the degree of transformation of the different phases and modifications of silica and of the varying degrees of porosities.

The same is true of the almost universally employed method of testing the resistance of refractory materials against temperature fluctuations, the quenching of the red hot bricks in running water, if this test is carried out without knowledge of the exact degree of burning to which the silica bricks have been subjected. The resistance of insufficiently burned bricks towards these excessively abrupt

¹ Technological Papers No. 116.

temperature changes is much greater than that of perfectly burned material, since the bonding substances have not been vitrified and sufficiently combined with the refractory bases to destroy their inherent power of resistance.

Silica bricks are very sensitive towards abrupt changes of temperatures, being but little superior to magnesite bricks, the least resistant of the common refractories. It is absolutely necessary, therefore, to treat these bricks much more carefully in this respect than is generally done in practical smelter work. Particular attention should be paid to this property of silica bricks at the lower temperatures.

Table 41 indicates the relative resistance of silica bricks against abrupt temperature changes as compared with the other refractories, the resistance of magnesite bricks being taken as 100.

In judging the sources of the various difficulties such as spalling and cracking, it is well to remember that the respective symptoms are not necessarily indicative of certain definite causes, but may be induced, directly or indirectly, by a number of other factors. For instance, while spalling may be caused by insufficient resistance against abrupt fluctuations of temperature or by excessive mechanical stresses, it is frequently due to heating up new furnaces too rapidly in the first place, the steam produced from absorbed moisture being generated too rapidly to permit of escape from the pores of the bricks, weakening the structure of the refractories sufficiently to cause spalling and cracking even at very moderate thermal or mechanical stresses. Similarly, chemical influences on the part of the products of reaction and the firing gases may prove to be the basic cause of spalling and—on the other hand—softening of the bricks which is commonly charged to excessively low melting or softening temperatures under load.

Acid gases and vapors as well as atmospheric oxygen, carbon, and the various metallurgical reducing agents do not attack silica bricks at any normal temperatures, while the resistance of silica refractories to the action of basic slags and oxides is comparatively low. It is for this reason, of course, that none of the white metals, such as lead, tin, and antimony, and their alloys may be melted in reverberatory furnaces lined with silica bricks, the oxides and slags produced dissolving the silica and forming silicates of the metals concerned. The same is true of all metals harmless themselves but containing metals forming corrosive oxides. For instance, in refining impure copper or cop-

per alloys containing lead or tin, only the hearth may be constructed of silica bricks while fire-clay or magnesite bricks should be used to line the sides and the roof of the furnace.

FIRE-CLAY BRICKS

Of the various types of refractory bricks employed in the residue and scrap treating industries fire-clay bricks are by far the most important quantitatively, their high resistance against the chemical and mechanical influence of the metals, oxides, gases, and slags as well as their exceptional mechanical resistance against abrupt temperature fluctuations and mechanical wear qualifying them for most metallurgical purposes. It is true that these advantages of fire-clay bricks are opposed by comparatively low softening and melting temperatures under heavy loads, but while in the first place, very few processes employed in residue smelting or scrap refining reach the minimum softening temperatures of high grade fire-clay bricks, it is not very difficult to meet this handicap by correct construction of the furnaces.

The various American fire-clay bricks are classified by the manufacturers as follows:¹

1. Flint-Clay Bricks, which are made with flint or semi-flint clay, predominating in the composition, and just enough plastic fire-clay to furnish the necessary workability.

2. Grog Bricks and Shapes: The outstanding characteristics of this class is the content of "grog" or pre-burned material. Since the grog has already been burned, it develops no plasticity when ground, has no drying shrinkage, and practically no burning shrinkage. Grog is used in practically all larger shapes and in many brands of bricks, and its continued use under controlled conditions is to be encouraged.

3. Plastic-Clay Bricks and Shapes: This classification is peculiar to products made of silicious clays from the New Jersey district.

4. Plastic-Clay Bricks, Dense Burned: Being made almost entirely of plastic or semi-plastic clay, the drying and burning shrinkages are relatively large and the drying and burning proportionally difficult.

The average composition of high-grade commercial fire-clay bricks is as follows:

¹ Liddell's Handbook of Chemical Engineering, 491-493.

36.0–41.0%	Al_2O_3
55.0–60.0%	SiO_2
0.8– 2.0%	Fe_2O_3
0.3– 0.7%	CaO
0.2– 0.5%	MgO

The specific gravity averages 2.5 to 2.7, the softening points under load should not drop below 2450° Fahr., while the average melting points range between 2700° and 3000° Fahr. The maximum alumina contents of natural raw materials used in the production of metallurgical fire-clay bricks do not exceed 46 to 47 per cent Al_2O_3 . Higher alumina contents are due to special additions for the purpose of raising the melting points of the refractories. For instance, while the melting point of a fire-clay brick containing 66.5 per cent silica, 28.0 per cent alumina and 1.8 per cent iron oxide is about 3000° Fahr. (without load), softening of the bricks under load commencing at about 2480° Fahr., the softening point of a fire-brick material containing 41.54 per cent silica and 55.44 per cent alumina is about 2600° Fahr.

Attention is called to the fact that all the softening and melting temperatures given apply to fire-clay materials under normal load, that is to say, the load to which the bricks are subjected within the metallurgical furnace. The figures usually given by ceramical and Government authorities, on the other hand, are obtained by testing isolated bricks and are therefore considerably higher. The following extract from the United States Government Master Specification for fire-clay bricks indicates this fact, besides giving some interesting data concerning other desirable properties of these refractories. No specifications seem to have been drawn up for metallurgical fire-clay bricks, but the class SH 75, applying to bricks for use under the most severe conditions of boiler practice, including severe vibrations, rapid changing of temperatures, and slagging and spalling influences, will doubtlessly conform to high grade metallurgical bricks, while the class H 75, applying to bricks suitable for ordinary boiler practice, and requiring a high degree of resistance to slagging, spalling, and high temperatures conforms to lower grade fire-clay bricks for use in melting pot furnaces, etc., or wherever the thermic, mechanical, and chemical stresses are not uncommonly heavy.

United States Government Master Specification for Fire-Clay Bricks (Extract).—The material covered by this specification is a

brick of standard or special shape composed of heat-resistant clay or clays and which has been burned to produce the desired strength and structure. The brick shall be compact, of homogeneous structure, free from checks, cracks, voids, or soft centers. All corners shall be sufficiently solid and strong to prevent excessive crumbling or chipping when handled.

All bricks of the standard 9-inch series shall not vary from specified dimensions more than one-eighth inch in width and thickness and three-sixteenths inch in length. For special shapes no dimension shall vary more than 2 per cent from the dimension specified unless greater variation is allowed by contract, but in no case shall a variation of less than one-eighth inch be specified, and they shall be free from such swells, warps, twists, or distortions as shall prevent ready and accurate laying up with a maximum joint of one-eighth inch.

Class SH 75.—The material shall contain not more than 65 per cent total silica.

The softening point shall be not less than that of standard pyrometric cone No. 31 (approximately 1650° C. or 3000° Fahr.)

The material shall withstand 15 quenchings without failure.

When specified the brick shall pass the simulated service test.

Class H 75.—The softening point shall not be less than that of standard pyrometric cone No. 31 (approximately 1650° C. or 3000° Fahr.).

The material shall withstand five quenchings without failure.

The absorption after reheating shall not be less than 6 per cent nor more than 16 per cent.

General Properties of Fire-Clay Bricks.—Although highly resistant in principle against the chemical influence of practically all acids, gases, and atmospheric oxygen, resistance of fire-clay bricks against chemical corrosion generally is appreciably decreased by large percentages of silica. Acid gases and vapors do not affect these bricks at temperatures below 2400° Fahr., while at higher temperatures resistance against corrosive attacks appears to be most pronounced with the more acid types of fire-clay mixtures.

On account of its direct bearing on the absorptive capacity of fire-clay bricks for gases, vapors, and slags, the degree of porosity is of principal importance in determining the chemical resistivity of these refractories. The higher the degree of density, the less pronounced the absorptive capacity. However, since, on the other hand, in-

creased density is also equivalent to decreased resistance to temperature fluctuations, recourse is often had to improving the surface density of porous refractories by glazing. Many suggestions have been offered towards the development of effective glazing methods, but no process has yet been devised which, while giving more or less perfect glazing effects, did not tend to seriously deteriorate one or several of the other important properties of refractory materials. All of these methods provide for the lining or washing of the bricks with substances of comparatively low melting points, which at the temperatures of the processes involved will either fuse into the surface of the bricks, or form a glazed coating over the surface proper. Many of the compounds suggested for this purpose are strongly alkaline chemicals which penetrate into the bricks, weakening their resistance to the influence of heat. Others form surface glazes which on account of their different coefficients of expansion chip off easily, roughening and weakening the surface of the bricks. Alkalies or similar glazing materials are not recommendable for use in metallurgical furnaces, and the only practical method of glazing fire-clay bricks is to treat the inside and outside surface, as far as the latter are also subjected to the objectionable effects, with a thin paste of finely divided basic mortar, containing not more than about 3 to 5 per cent of soda or potash. Best results are obtained if this paste is sufficiently thin to require two or three paintings, which are burned-in each at a time.

The resistance of fire-clay bricks to abrupt changes of temperature is governed by the structure and density of the material as well as by the thermal conductivity and the coefficient of expansion. Of the common metallurgical refractories fire-clay bricks are by far the most resistant. The extent of the influence of the silica contents of the fire-clay brick on the resistance of the material against temperature fluctuations, although established beyond doubt qualitatively, is still a matter of argument. Modern metallurgical and ceramical research and practical experience have shown, however, that this resistance decreases with increasing percentages of silica. For most metallurgical purposes a fire-clay brick containing 45 per cent clay gives best results, while fire-clay containing 30 per cent clay and 60 per cent quartz proved to be the least resistant.

The resistance of fresh, unused fire-clay bricks towards mechanical stresses and erosion is of more or less theoretical interest only,

since this property is decisively influenced by operating conditions. All factors tending towards the formation of cracks, etc., lower the mechanical resistance of the refractories. The higher the furnace temperatures—up to a certain maximum value—the lower the resistance of the fire-clay bricks towards erosion and impacts. On passing this maximum, the strength of fire-clay materials rapidly decreases until initial softening of the bricks precludes further mechanical resistance of the masonry.

Of the various grades of common American fire-clay materials, high grade flint-clay and grog bricks are the most refractory and the most resistant to spalling, although regarding some other important properties, such as deformation under load and resistance to abrupt temperature fluctuations at the higher temperature ranges, these bricks do not give quite as good results as the open burning siliceous plastic clay bricks.

Andalusite.—Large deposits of highly refractory andalusite deposits have been located in California, and the indications are that the use of this material in the production of refractory bricks will prove highly interesting for metallurgical purposes. An average analysis of California andalusite showed the following composition:

56.89%	Al_2O_3
33.78%	SiO_2
0.37%	H_2O
3.67%	loss by ignition
5.37%	undetermined constituents.

The melting point of this material is very high, and bricks made from high-grade andalusite material do not change shape or volume at comparatively very high temperatures. Its coefficient of expansion being very low, andalusite brick material is also very resistant against abrupt temperature fluctuation. Compared with high-grade fire-clay bricks, andalusite bricks stand up much better under high temperatures and heavy loads. Comparative tests have shown that while at certain temperatures and loads the degree of compression suffered by high-grade fire-clay bricks amounted to 4.36 per cent, that of the andalusite brick tested did not exceed 0.38 per cent.

MAGNESITE BRICKS

The most important advantage possessed by magnesite bricks as refractory material for metallurgical purposes is their high melting and softening temperatures and their chemical indifference towards basic, neutral and most acid influences, even at comparatively high temperatures. The melting temperatures of good average magnesite bricks range from 3800 to 4000° Fahr., although the softening temperatures under maximum loads are appreciably lower, fluctuating between 2600 and 3000° Fahr. However, by decreasing the amount of silica contained in the natural magnesite, a process accomplished by electro-magnetic separation, the softening temperatures are raised considerably.

Technical magnesite bricks are almost exclusively manufactured from crystalline raw magnesite (magnesium carbonate) which is sintered at temperatures ranging from 2700 to 2900° Fahr. Pure magnesite materials are never used for this purpose, since the natural magnesite ores, containing varying percentages of iron oxide, clay, lime, and silica, induce the sintering properties required without appreciably decreasing the melting and softening points. The exact percentages necessary to confer the desired sintering properties depend upon the respective physical and chemical characteristics of the refractory material treated.

The most important of these impurities is iron oxide, which in good magnesite ores is present in percentages of up to 8 per cent and which is needed to confer sufficiently satisfactory sintering properties. If iron oxide is not contained in natural raw material, it must be added in sufficiently large quantities to attain the desired results. It is for this reason that the purest magnesite deposits are really the least desirable and that the common magnesite grades mined in California, Steiermark, Veitsee, Hungary, and India are generally preferred as refractory raw material to the much purer magnesite mined at Euboea, Greece, which, instead of sintering, crumbles at the normal sintering temperatures of magnesite. The same is true of the comparatively pure magnesite deposits located in the state of Washington, and pure iron ores are therefore added to the raw mixtures in suitable quantities. About 4 to 8 per cent of iron oxide is required for satisfactory sintering. On burning the bricked mixtures at high temperatures, magnesium ferrite ($\text{MgO} \cdot \text{Fe}_2\text{O}_3$) is formed, and this compound is chiefly responsible for the sintering of the magnesia bricks.

The total impurities contained in the calcined products of some of the important deposits are:

TABLE 39

	CaCO ₃	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂
	Per cent	Per cent	Per cent	Per cent
Steiermark.....	1.76	7.79	0.82	3.40
Greece.....	0.83-10.92	0.56	3.52	0.70-7.10

The analysis of magnesite bricks of Austrian, American, and Greek origin have been reported as follows:

TABLE 40

	MgO	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO
	Per cent	Per cent	Per cent	Per cent	Per cent
Steiermark.....	85.31	Tr.		9.05	4.70
U. S. A.....	87.66	1.19	8.10	1.19	2.05
Greece.....	86.66	3.76		6.64	3.10

The refractoriness and durability of magnesia bricks is considerably higher than the respective properties of silica and fire-clay bricks, but these advantages are accompanied by a few important disadvantages which disqualify the bricks for a large number of metallurgical purposes. The chief disadvantages of magnesite bricks are:

1. A high degree of brittleness in the cold state,
2. A comparatively low resistance to abrupt temperature fluctuations,
3. On continual heating at elevated temperatures magnesite develops a high degree of brittleness, apparently due to the peculiar crystalline nature of the magnesite.

While the excessive brittleness of magnesite bricks in the cold state is of small importance in actual metallurgical practice, it represents a factor of serious economical consideration in the construction of furnaces, since even with experienced and highly specialized masons the breakage incurred in shaping and laying magnesite bricks considerably exceeds that suffered with any other of the common refractories.

The most serious practical disadvantage of magnesite, the low resistance to sudden temperature fluctuations, can only be countered by careful control of furnace temperatures during and after operations involving elevated temperatures. Table 41 indicates the relative resistance of magnesite bricks to sudden temperature changes, as compared with the other refractories, the resistance of magnesite bricks being taken as 100.

TABLE 41

Magnesite Bricks.....	100
Silica Bricks.....	75
Chromite Bricks.....	42
Fire-clay Bricks—first grade.....	3 to 10
Fire-clay Bricks—good grades.....	10 to 15
Fire-clay Bricks—lower grades.....	15 to 30
Zirconia Bricks.....	16
Bauxite Bricks.....	13
Carborundum Bricks.....	2

This lack of resistance to sudden changes of temperature displayed by magnesite bricks is shared by all other refractories containing high percentages of magnesite, including the so-called basic refractory washes recommended for the protection of high temperature furnace linings. While most of these washes are very effective in protecting the refractory masonry against the penetration of vapors and gases, they will crumble within a comparatively short time after being subjected to the ordinary high temperature furnace routine.

Thus, it is obvious that the operation of magnesite-lined furnaces can be rendered economical only, if due attention is being paid to perfect equalization of temperatures, that is to say to the maintenance of practically similar temperatures for as long periods as are compatible with efficient operation of plant. All changes of temperatures must be gradual, and variations of temperatures within the different sections of the furnaces should be avoided by all means. As long as the interior of the furnaces is bright red-hot, admission of small quantities of cold air through the working doors does not do any appreciable harm, although a steady flow of cold air across a certain section of the lining should be guarded against.

Whenever an empty furnace lined with magnesite bricks is to be cooled down, the red hot bottom should be covered with a layer of coke fines about 3 or 4 in. thick and all doors closed and luted with fire-clay. The door of the ash-pit as well as the flue channel should

also be closed or blocked so as to prevent undue cooling of any part of the magnesite lining.

The bottoms of lead refining furnaces, which are frequently lined with magnesite bricks, may be protected very efficiently by maintaining a constant layer of lead. The tapping hole is raised about 2 or 3 in. above the centerline of the hearth—the exact height being governed by the curvature of the bottom—so that the whole of the hearth is always covered by a correspondingly thin layer of lead which protects it against too rapid cooling as well as against mechanical stresses imposed by careless charging of the heavy slabs composing the next charge. It appears to be good practice in this case after tapping the furnace to cover the remaining lead with a heavy layer of coke fines.

The electric conductivity of magnesite bricks is very low, while the thermal conductivity is comparatively high. The melting points of high grade bricks are very high, ranging from 3800 to 4000° Fahr. However, since at somewhat lower temperatures the iron compounds present commence to vaporize, the chief bonding agents are gradually removed, and the bricks begin to crumble. This reaction is indicated by a distinct bleaching of the brick surfaces. The softening temperatures of magnesite bricks under load are considerably lower than the melting temperatures, even if, by removal of part of the silica contents, a certain improvement may be obtained, a fact which must be seriously considered in selecting the lining materials for metallurgical furnaces.

Application of Magnesite Refractories in Furnace Construction.

—It appears certain that the lining of lead-refining furnaces with magnesite bricks represents a distinct technical and economical error usually induced by unfavorable results obtained with fire-clay bricks. It is a well known fact, however, that fire-clay bottoms of lead refining furnaces will cause serious trouble only with faulty brick material or careless laying. The author has seen many lead refining bottoms built of good quality fire-clay bricks and laid with proper care which were over two years old and still in perfect condition. In several cases where, apart from perfect laying and efficient furnace operation, the bottoms were kept covered with a layer of lead at all times, the furnaces showed no sign of trouble after 3 years of constant operation. It is clear that even the best of magnesite bricks would never stand the extraordinary stresses connected with lead refining operations for nearly as long periods—in spite of their much higher costs.

Copper refining furnace bottoms are rarely lined with magnesite bricks, although these are often employed for lining a narrow section of the walls between the silica lining of the lower parts of the walls and the upper section of the furnace. In America, the entire upper section of the copper refining furnaces is usually lined with magnesite bricks, the lower parts of the walls, up to the surface level of the metallic bath being lined with silica brick, while in order to prevent the fluxing of the acid and basic linings at their line of contact, two or three layers of chrome bricks are usually interposed. Lining the upper section of the walls and the roof of copper refining furnaces with magnesite bricks is advantageous in that this material is much more resistant against the corrosive action of the spattered copper particles, containing large percentages of copper oxide, which would seriously attack silica linings. Fire-clay bricks are equally resistant, of course, but they are not sufficiently refractory for this purpose.

Considerable use is made of magnesite bricks for the linings of bronze and brass reverberatory furnaces, and it has been shown that high-grade magnesite bricks carefully laid give very satisfactory results. The life of magnesite bottoms of these furnaces may be considerably lengthened if they are treated with basic slag or, even, glass scrap at white heat. Care must be taken, of course, not to use too much of this material since, while sintering the whole magnesite bottom into one solid block if used with discretion, its resistance and compactness may be entirely destroyed if the fluxing agents are used in excess. As a rule, a few hundred pounds of glass scrap are spread out over the bottom, and additional material is only added if, after maintaining a white heat for a short time, all of the glass has been absorbed, the amounts added never exceeding 20 or 30 pounds. Since the melting point of the magnesite-glass mixture is comparatively high and the working temperatures of the brass and bronze furnaces are not supposed to ever reach white heat, the bottoms thus produced are exceedingly tough and elastic, while absorption of valuable metals by the hearth is reduced to a minimum.

The mortar employed in laying the bricks consist of finely ground calcined magnesite made up to a thin paste with tar or linseed oil, but much better results are often obtained by laying the magnesite bricks in dry magnesite mortar. It is obvious, of course, that with dry laying the bricks must be of absolutely accurate shape and nicely finished.

CHAPTER XIX

CRUCIBLE FURNACES

Crucible furnaces are generally employed for melting comparatively small quantities of metals or alloys, which on account of excessively high melting points or strongly corrosive properties cannot be treated in iron or steel melting pots. In a number of instances, as, for example, in melting aluminum or its alloys, crucible furnaces and melting pots are used side by side, although in this and similar cases correctly constructed crucible furnaces will doubtlessly produce cleaner metals.

Crucible furnaces may be heated by coke, gas or oil, while in recent years electrically heated crucible furnaces have been developed. The number of crucible furnaces heated by oil or gas is steadily increasing, although the type of furnace most generally employed at present is the tilting, coke-fired air-blast pit furnace. The older types of crucible furnaces, particularly the crucible shaft furnaces, with natural draft, are not nearly as efficient, giving rise to greater loss of metal by oxidation and to the production of comparatively impure metals, as well as to greater wear and breakage of crucible materials.

Crucible furnaces of the older makes are rectangular chambers lined with fire-clay bricks, provided at the bottom with fire bars, and connected near the top with a chimney—or shaft—by means of a more or less inclined flue. Several of these furnaces are usually arranged in a row at the floor level, the flues connecting with a main flue, which conducts the waste gases into the stack. In front of these furnaces are the ash pits covered by strong gratings. The crucibles are not placed directly on the bars in order to prevent the chilling of the bottom layer of metal, but on a brick support, usually a fire-clay brick placed on the bars. Occasionally, the crucible is placed on the bed of coke in order not to reduce the available free grate space, but this method is decidedly faulty, since the crucibles will not remain in the same position and may even lead to the loss of metal or dross by splashing. Arched supports may be used instead of flat brick supports, which do not seriously interfere with the passage of air.

The size of the furnace is determined by the height and diameter of the crucibles. For pots of smaller types, holding about 150 pounds of metal, the furnace chamber should be made about 18 inches square and not less than 4 feet deep. The chamber must be wide enough to have a 4-in. layer of ignited coke around the crucible. The lower edge of the flue opening should be about 4 to 6 in. above the crucible rim, so as to prevent chilling of the surface of the bath by the cold air drawn through the furnace top. Another important factor determining the depth of the crucible furnace chamber is the thickness of the coke layer beneath the crucible, which should suffice to use up all the oxygen contained in the air. It is obvious that if this is not the case, correspondingly larger amounts of air must be drawn through the coke bed, resulting in lower heat efficiency.

The proper construction of the flues is of eminent importance in deciding the temperatures attainable in the chamber. While the exit flue must be made large enough to take care of all the draught required to convert the carbon into carbon dioxide within a sufficiently short space of time, it must be restricted to the minimum cross-section necessary to attain this end. The object of the flue is not to produce as strong a draught as possible, but to attain maximum temperatures and to hold this heat around the crucible as long as is possible without causing too strong a contamination of the flue gases with carbon monoxide. To adapt the section of the exit flue to that of the fireplace is only advisable with crucible furnaces of exactly the same construction, since it is not the total grate area but the free air space of the fireplace which determines the volume of the air of combustion drawn into the chamber. While in correctly constructed crucible furnaces the firebars are thin and deep, providing for a maximum area of free air space, the furnaces constructed in smelting works are usually equipped with simple rectangular or square iron bars laid on a pair of cross-bars, the free air space in this case being reduced to only a fraction of that provided by thin and deep bars. For melting non-ferrous metals and alloys, the exit flues of single pot furnaces may be made from 6 by 3 in. to 9 by 4 in.

It is not generally recognized that the shape of a crucible furnace exerts a considerable influence on the heat efficiency, circular furnaces being more efficient in this respect than square ones. This is due to the fact that the crucible is heated only by the coke with which it is in direct contact, the radiation of the layers of coke further removed being prevented from reaching the crucible walls by the high degree

of opacity of hot coke to heat radiation. Thus, since the coke located in the corners of a square crucible furnace chamber has no direct part in heating the crucible, and since its influence in maintaining the general temperature of the furnace is not only negligible but more than neutralized by the larger surface of a square shaped furnace of equal capacity, single-crucible furnaces should be circular in cross-section. Applying these deductions to twin-crucible furnaces, elliptical furnaces are more efficient than rectangular types.

The chamber of crucible furnaces is usually made of highly refractory fire-clay bricks of single thickness held together by iron stays and ties. Circular chambers should be constructed of shapes, requiring as little cutting as possible. The methods of setting and laying the bricks is identical with those to be applied for reverberatory furnaces, etc. If the walls of the chamber are not air-cooled—by drawing the air of combustion through an outer space surrounding the walls of the combustion chamber on all sides—the brick walls are often lined with ganister or similar material, which is stamped into place between the walls and a wooden core shaped to conform with the size and shape of the chamber.

The position of crucible furnaces relative to the floor level depends upon the size and capacity of the units. If the crucible capacity does not exceed 75 to 100 pounds, the furnace top should be about 20 to 25 inches above floor level, while furnaces of larger capacities should be located below floor level, so as to have the furnace top level with the working-floor, facilitating the handling of the hot crucible and the other manipulations involved in the operation of the crucible furnace plant.

The chief disadvantages of this type of crucible furnace are the difficulty connected with the handling of the hot crucibles during casting, and the deteriorating influence of regularly occurring abrupt changes of temperature on the strength of the crucibles. The lifting and manipulation of the crucibles during casting may be facilitated to some extent by employing tongs manipulated by chain tackle hung from the roof over each furnace, or a traveling arrangement where a number of furnaces are arranged in a line, but the casting from crucibles is tedious and inefficient as long as the crucible must be removed from the furnace.

Figure 51 shows a common construction of this type of crucible furnace plant.

A certain degree of improvement is effected by heating the cru-

cibles with gas instead of solid fuel, the construction of the furnace proper remaining practically the same. Figure 52 shows an arrangement formerly used at the Berlin Porcelain Manufactory, and in the Mint.¹

A is a chamber of fire-brick having an ordinary flat grate, composed of iron bars, and another grate in which the bars are placed in steps b. On a grate of this kind small free-burning coal may be used, which would be rather too small for ordinary grates. By this arrangement of bars, the surface of the grate is considerably in-

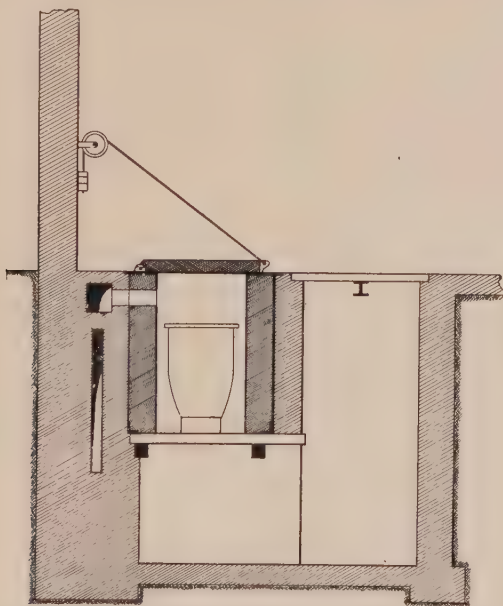


FIG. 51.—COMMON TYPE CRUCIBLE FURNACE PLANT.

creased and ample space allowed for the admission of air. A blast of air is introduced under the grates by the pipe f. The two openings, d, e, are closed by iron doors. The fuel is charged through g and h, the gases generated, consisting chiefly of carbon monoxide, passing through the pipe k, which is provided with a regulating valve l.

At m the gases meet air issuing from pipe n, the carbonic oxide is burned, and the heat is communicated to the furnace in which

¹ Hiorns, *Mixed Metals*, p. 179.

the crucible is placed. In order to represent both the gas producer and the melting furnace in the same vertical section, it has been necessary to deviate from the actual position of these furnaces at the mint, where the melting furnace is at the side of the gas furnace. The air is forced by a small fan through the pipes *f* and *n*, which are provided with regulating valves.¹

Attempts to avoid the chief disadvantages of this type of crucible furnace connected with the periodical removal of the red hot crucible

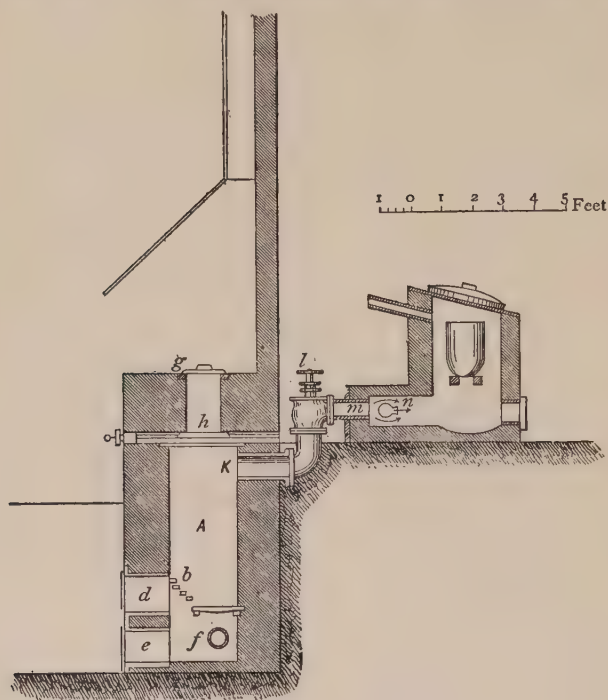


FIG. 52.—OLD GERMAN CRUCIBLE FURNACE PLANT.

from the furnace have been made more than 50 years ago, the first successful solution of this problem being the crucible furnace constructed by Piat about 1880. The original Piat furnace exhibited a considerably stronger casing and was suspended by means of trunnions. The crucible was held in place by a tile. On finishing a melt, the metal was poured without taking out the crucible. Apart from prolonging considerably the life of the crucibles, the Piat furnace

¹ Percy, Metallurgy, p. 201.

made possible the use of larger charges, since the size and capacity of the crucibles ceased to be determined by the limited resistance of the hot crucible walls to the heavy stresses incurred by their direct handling by means of tongs.

Another early crucible furnace construction of this type was the Baumann furnace, the improved form of which is still being used in a number of foundries and melting works, in this country and in Europe. The furnace is encased in a heavy sheet iron mantle and is operated by a comparatively clumsy mechanism, consisting of a heavy lever operating two supporting rods at one end and forming a toothed sector at the other. This sector engages with a pinion rotated through a worm gear and rod by means of a handwheel. By moving the sector downward, the opposite end of the lever forces the supporting rods upward, lifting the furnace up and into a horizontal position. The author has worked with a number of Baumann furnaces in a South German smelter, but did not derive much satisfaction from their use. While operating satisfactorily in a general way, the operating mechanism is exceedingly unwieldy. A battery of three units requires a pit about 6 feet deep, 24 feet long, and 12 feet wide. The lever with the toothed sector alone weighs several hundred pounds, and two heavy foundations are required to carry the furnace and the operating mechanism. There are any number of modern makes of tilting crucibles, which give similarly good service without requiring nearly as large a space and as heavy a general equipment.

The general efficiency of coke fired crucible furnaces is considerably improved by working with forced draft, which enables the melting of much larger charges in one third or one quarter the time required by ordinary coke fired crucibles, and at an appreciably smaller consumption of coke.

The first crucible furnace operating with forced draft was the well-known Piat-Baumann furnace, which embodies practically all the principles applied in the construction of modern furnaces of this type. These furnaces are supplied with preheaters and are suited only for metals or alloys with high melting points. They are not well qualified for the treatment of aluminum, or for other white metals and alloys liable to excessive oxidation at comparatively low temperatures.

Modern tendencies being toward the development of light and easily operated tilting furnaces of large operating radius, crucible

furnaces for general use in white metal or aluminum foundries and melting works are now being taken out of the pits and placed on floor level. While the majority of these furnaces are stationary, a

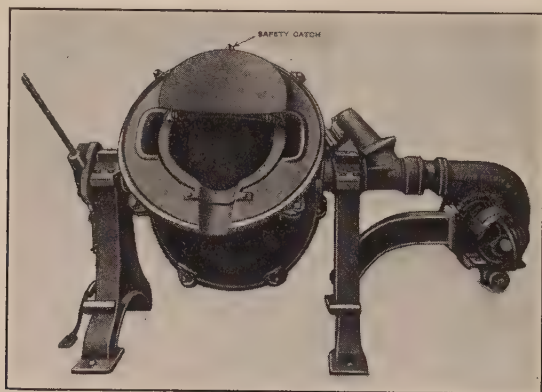


FIG. 53.—TILTING TYPE CRUCIBLE FURNACE (Hausfeld).

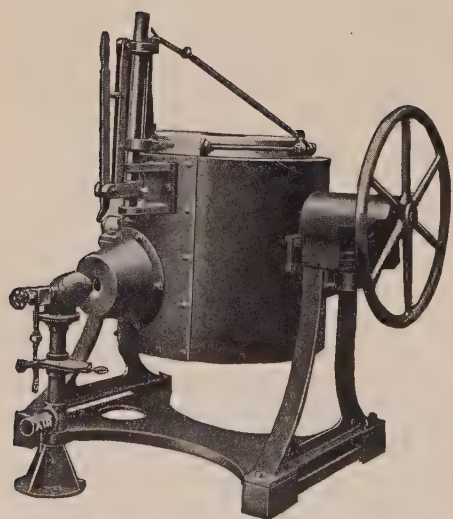


FIG. 54.—TILTING TYPE CRUCIBLE FURNACE (Monarch).

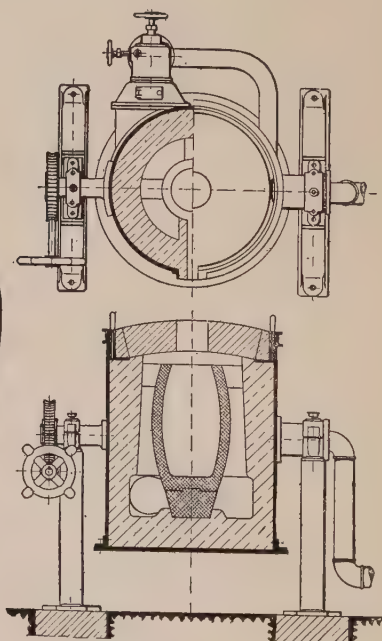


FIG. 55.—GERMAN TILTING TYPE CRUCIBLE FURNACE.

number of makes have been placed on wheels in order to increase their operating radius. Some of the latter types of furnaces are coke fired while others are heated with oil or gas, although in this case the furnace must always be returned to its original position after casting.

Figure 53 represents a Hausfeld Tilting Type crucible furnace for natural or artificial gas, fuel oil or kerosene. The legs and trunnions are cast iron. The drum is well balanced and the long handle affords ample leverage for easy manipulation while the locking mechanism enables convenient release or engagement by foot pressure. Attention is called to the convenient cover lifting device, which

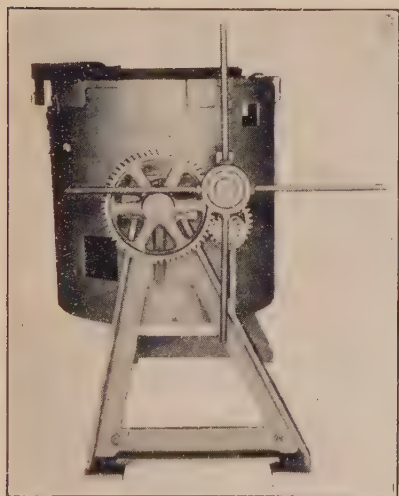


FIG. 56.

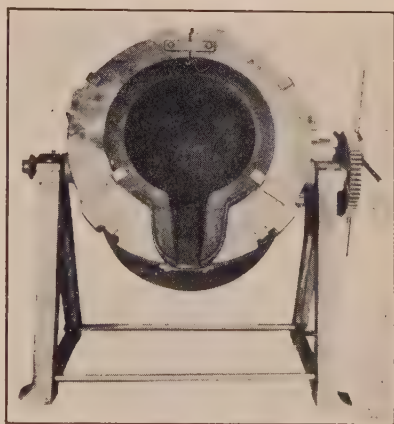


FIG. 57.

FIGS. 56 AND 57.—TILTING TYPE POT FURNACE.

is supported on the leg of the furnace independent of the furnace drum, enabling the operator to tilt the furnace with the cover brick on or off at his option. When the cover brick is placed on the furnace it is automatically locked in place.

Figure 54 shows a modern tilting Monarch crucible furnace heated by oil or gas.

Figure 55 represents a stationary tilting oil fired crucible furnace of German origin.

A special type of tilting melting furnaces has been developed

for the melting and remelting of aluminum, a cast iron melting pot being used as container instead of graphite crucibles. Figures 56 and 57 illustrate an Aluco tilting type aluminum melting furnace using a cast iron melting pot of special composition.

Aluminum melting furnaces of this type are the only small capacity melting unit generally employed in white metal and aluminum melting plants, while crucible furnaces in general are used for the production of base metals required for the manufacture of white metal or aluminum alloys containing copper or other metals of comparatively high melting points.

CHAPTER XX

MELTING CRUCIBLES

Practically all melting crucibles used in modern non-ferrous smelters and foundries today are made from mixtures consisting chiefly of large flaked graphite, or plumbago, mixed with clay and small percentages of sand. High-grade graphite crucibles contain at least 60 per cent of large flaked graphite which is most resistant against the oxidizing influence of the flames and which decreases considerably the porosity of the crucible material.

The advantages offered by graphite crucibles as compared with clay crucibles are not only the considerable improvement of the various important mechanical properties, but also their high coefficient of thermal conductivity which, apart from inducing a correspondingly higher degree of heat efficiency, prevents undue stresses within the crucible walls as caused by the differences of temperature prevailing in the various sections of the crucible.

Besides, there are a number of metals and alloys, such as aluminum and its alloys, which exert a distinctly corrosive influence on straight clay materials, acid and basic, while the development of other types of highly refractory and chemically resistant crucibles as, for instance, magnesia-alumina or zircon dioxide crucibles, has not been carried far enough to be of practical value to the smelting and foundry industries.

Treatment of Fresh and Used Graphite Crucibles.—Apart from the influence of the nature and quality of the constituents of crucible mixtures, their resistance against wear is governed by the treatment accorded. Indeed, it may be stated, that in a large percentage of smelters and foundries the comparatively low number of heats obtained are solely due to inefficient and careless treatment of new and used crucibles.

It should be remembered in the first place that on their arrival at the plant, the crucibles are but weakly burned and dried, the crucible material being very hygroscopic in nature, absorbing moisture readily even in warm and comparatively dry rooms. This moisture is tena-

ciously held by the crucible material and must be driven out as slowly as possible in order to avoid cracking of the fragile structure. It is absolutely imperative, therefore, to unpack the crucibles as soon as received and store them in a warm and absolutely dry place free from draught.

The practice of placing the crucibles on top of reverberatory or annealing furnaces is faulty in that it exposes them to frequent temperature changes and to the influence of the cold draught. It is worse than useless, of course, to expel the moisture contained in the crucible walls during day time, only to have it re-absorbed on cooling the furnace over night. Much better results are obtained if a fairly isolated place between two or more active furnaces is available where the crucibles are subjected to a reasonably even warm and dry atmosphere practically free from draught. Crucibles should never be stored on the ground, however, so that even in this case it is best to place them on boards resting on bricks, etc., so as to be removed from the ground sufficiently far to preclude the danger of soaking the crucible bottoms full of moisture.

Crucibles should never be stored in furnaces or other drying appliances used for the drying of smelter or foundry materials, such as cores, etc., the moisture generated being taken up by the crucible material in spite of the comparatively high temperatures involved.

By far the best results are obtained if the plant is provided with a regular crucible drying oven heated by steam or flue channels. These storage ovens represent inexpensive pieces of equipment and may therefore be installed in any smelter or foundry using more than two or three graphite crucibles a month. It is not necessary, of course, to construct a standard furnace requiring a certain amount of valuable floor space, but the drying appliance may simply be erected on dead, unused space between or behind some active furnaces, or even on top of some other drying furnace, such as core ovens, where an even, low heat is being maintained.

The drying chamber may be constructed by simply bolting or riveting together a few sheets of iron, the measurements of the chamber depending entirely on the average number of crucibles stored. If floor space is a deciding factor, the chamber may be built high enough to take up 4 rows of crucibles, which are stacked two high, open end to open end, with a wooden board between each layer to permit of free circulation of air within and around the crucibles. For ventilation and removal of the moisture generated, a number of

holes should be provided at the lower part of the ends and sides of the chamber. Ventilation apertures in the roof of the ovens will permit of an excessive exit of warm air, while the specifically heavier damp air will remain at the bottom.

Annealing the Crucibles.—In annealing the dried graphite crucibles, the rise of temperature to redness should be effected as gradual as possible. New crucibles are placed in a cold furnace and the temperature is raised very gradually until red heat is reached, when the crucibles may be charged and put to work. It will also prove of advantage to preheat the first charge by placing the metal on top of the furnace cover, a method which applies to the full charge—not to the first few pieces of metal only—since putting the cold metal into the molten bath may result in a chill-back, causing cracking of the fresh crucibles.

Painting and Lining of Crucible Walls.—To increase the resistance of crucibles to the oxidizing effects of the firing gases and to diminish the penetration of the products of combustion through the walls, the outside of the crucibles may be painted with fluxing materials. A very efficient material for this purpose is a pasty mixture of finely ground crucible substance and water glass with about 3 to 5 per cent of soda ash. The proper consistency and composition of this mixture depends upon the kind and composition of the particular crucibles used and upon the melting processes involved, and must be determined by experience. It should be fusible enough to conglomerate the graphite, silica, and clay particles composing the surface of the crucible mass, without entering and vitrifying the structure. The paste is applied about three times to achieve the desired result, each coating being dried before applying the next one.

This treatment is applicable only with oil or gas fired furnaces, but is absolutely harmful with coal or coke fired pit furnaces, since the glazed surface, which is softened by the high local heat of the glowing coke, is rapidly removed by the abrasive effect of the solid fuel.

The interior of the crucible walls cannot be treated the same way, of course, since the caustic, fusible glaze will be removed by the softening and abrasive influence of the metallic bath as well as by the still more effective fluxes and slags. The only suitable interior lining of crucibles must therefore be composed chiefly of refractory materials moistened and held together by chemically inactive and non-fusible substances. As a rule, the frequent application of a thin coating of

ordinary graphite blackening, such as used in the foundry, will prolong the life of graphite crucibles considerably. Another suitable coating consists of finely ground magnesite calcined at high temperatures which is made up to a fine paste with common molasses. After applying this coating, it is carefully dried a few days and the crucible brought gradually to red heat. On cooling, the cracks formed by the first heating period are closed up with fresh paste and the crucible is dried and heated again.

There are a number of other interior crucible coatings suitable to certain processes which are of no avail if used for any other melting process. For instance, a very efficient protective coating may be applied to graphite crucibles used in the melting of aluminum by painting the interior of the crucibles with aluminum bronze varnish which is oxidized under the influence of red heat, forming an absolutely neutral surface towards fused aluminum.

General experience has proven that careful drying and annealing of graphite crucibles together with the protective influence of exterior and interior coatings will improve the active life of crucibles at least 50 per cent.

Crucible Tending in General.—Graphite crucibles should not be charged while cold. The outside of the crucibles would then be heated to redness long before the inside of the walls, the heat of which is rapidly conducted away by many cold metals, particularly aluminum, thus giving rise to internal strains and the formation of cracks. Ingots and other heavy pieces of scrap metal should not be dropped into the crucibles, but are placed into the crucibles in such a manner as to avoid wedging, since the appreciably higher expansion coefficient of the metals will cause the cracking of the crucibles.

All scrap materials are to be carefully examined for moisture. Tube material, valves, etc., are particularly liable to contain enclosed water pockets, and should therefore be opened and dried by preheating.

The use of fluxes, especially of alkaline nature, should be limited to instances rendering their presence absolutely necessary. Under no circumstance, however, should fluxes of any kind be melted in empty crucibles.

“Soaking” a melted charge must be avoided. The metal is poured as soon as melted and heated to casting temperatures. The hot crucible is not to be placed on the cold ground, but in a sufficiently deep bed of dry white sand.

On pouring, the crucibles must be completely emptied of fused metal. It is stupid to leave the crucibles cool off half filled with metal. Every intelligent person knows that all metals and alloys will shrink on cooling, and since this shrinkage will not commence until all metal has solidified—in fact, most metals expand immediately previous to solidification—large surface sections of the crucible walls are torn off.

Tongs and shanks should make a perfect fit with the crucible, since in view of the decreased strength of the crucible walls at red heat, uneven pressure on the walls may cause cracking or leakage.

It is necessary for the same reason to remove accretions, such as pieces of coke or slag adhering to the outside of the crucible walls, especially at the section in contact with the tongs or shanks and at the bottom. Crucibles should be returned to the fire as soon as the metal is poured while after pouring the last charge, they should be returned to the warm furnace to assure of as slow and gradual a cooling of the crucibles as possible. This precaution will prolong the life of the crucibles at least 100 per cent, while savings of 250 to 400 or even more per cent have been reported by various operators.

About three years ago, The New York Brass Foundry, which used No. 45 size crucibles and gas fuel and melted red and yellow metal as well as 85-5-5 metal, introduced this method of protecting the crucibles against abrupt temperature changes. Before this period the best average of this company was 40 melts per crucible, taking off 10 to 14 heats a day at 35 to 45 minutes per heat, while on handling the crucibles by the method indicated the numbers of heats rose to above 150 per crucible, using No. 45 Dixon Vitrified pots. One of these pots was found to be in good condition after running 196 heats, while another went 275 heats. The reason for this unusual number of heats is that, apart from the many heats per day taken, the pots are never allowed to cool quickly but are returned to the hot furnace at night.

The cold crucibles should be examined for surface defects. Partial covering of the walls with slag is dangerous and must be carefully removed. A uniform coating of slag, on the other hand, increases the longevity of the crucibles and should not be disturbed. Deeply corroded parts of the crucible walls should be patched immediately with finely ground crucible mass made up to a thick paste with water glass. Patching is followed by slow and gradual heating of the crucible to bright red heat in order to fuse the patching mate-

rial on to the crucible walls. It is clear, of course, that the part to be patched must be carefully cleaned and freed from all metallic and vitreous accretions.

Relation of Graphite Crucibles to Fuels.—If solid fuel is used, this must be absolutely dry, since presence of steam causes formation of hydrogen and scalping of crucibles. The presence of an excessive amount of sulphur also will cause premature failure of graphite crucible.

If liquid or gaseous fuels are being used, crucibles are to be subjected to radiated heat only. The flames should pass along the round furnace walls, which must be absolutely smooth and free from obstacles, since wherever the flames are reflected from the walls at a sharp angle against the crucible, deep corrosions are produced in the ascending direction of the flames. The obstacles may be caused by deposits of soot in small crevices of the furnace lining, and may be removed by changing the direction and—occasionally—the nature of the flames.

Another form of corrosion, characteristic only of oil-fired crucible furnaces, consists of honey-comb shaped indentations at the lower section of the crucible walls due to oxidation of the graphite particles, the structure of the refractory constituents of the crucible material remaining practically untouched. It is impossible to avoid this difficulty entirely, since in burning oil, a certain excess of air is required to assure of complete combustion and to avoid the formation of soot. Gas fired furnaces do not greatly suffer from this defect if the furnace is operated correctly. It is a matter of experience that Ceylon crucibles or crucibles that contain sufficiently large amounts of Ceylon graphite are least subjected to this phenomenon, since, besides being more refractory than most other graphites, its thermal conductivity is very high.

The principle of indirect heating of graphite crucibles is interpreted by some manufacturers of crucible furnaces to simply mean that the flames of burners should not impinge upon the crucible walls. Accordingly, the crucibles are placed on comparatively high base bricks and the flames directed against this base, flowing upward and around the crucible walls. It is clear from the above deductions that the true principle of indirect heating is not correctly applied in this case.

CHAPTER XXI

DESIGN AND CARE OF IRON AND STEEL MELTING POTS

The working efficiency of a white metal foundry and the longevity of its units depend not only upon purely metallurgical consideration, such as the nature of the materials treated and the process involved, but are to a large extent influenced by the quality, sizes, and shapes, of the melting pots used, on the treatment and care of the pots during operation and at rest. While the metallurgical aspects of the numerous melting pot processes and their improvements have always found the interest of metallurgists, very little attention is usually paid to the other factors above enumerated, resulting in decline of general efficiency of plant and units, and in premature ruin of pots and furnaces.

Compared with reverberatory furnaces, melting pot furnaces are relatively cheap, they do not take up much space, and do not require trained and skillful operators. They are easily and quickly built. Their heating and operating efficiency compares well with that of reverberatory furnaces, and the loss of metal by fuming is comparatively insignificant.

The exceedingly heavy stresses to which melting pots are frequently subjected demands the choice of materials that will withstand for as long a time as possible the strong mechanical and chemical actions concentrated upon them. The most commonly used material for melting pots has always and everywhere been grey iron, which, for certain purposes, such as the production of small quantities of tin solder, gives fairly good service—not because grey iron is an exceptionally suitable material, but because almost anything will do for this purpose.

Where large quantities of white metal are produced, and a large scope of action is desired, grey iron should not be used as a material for melting pots. The deficiency of common grey iron for this purpose has long been recognized, of course, but no decided measures have ever been taken by the industries concerned to change the age-

old custom. The excuse usually offered by small smelters is that the foundry entrusted with the casting of their material is not prepared to cast anything but cast iron, or that the expenses incurred in having the pots made from special mixtures do not compare with the limited advantages obtained. There can be no doubt, however, that, apart from the much longer life of such melting pots, the greater purity of the metals treated should be sufficient inducement towards this timely change of policy.

The above deductions concerning the value, or lack of value, of grey iron pots in the white metal foundry, apply to white metals and zinc only. There are a number of groups of other metals or metallic alloys, such as aluminum and aluminum-zinc alloys, where ordinary grey iron pots give better service than special mixtures or, even, steel pots. It has been shown in the chapter on the treatment of aluminum scrap that the absorption of iron by aluminum at higher temperatures decreases with increasing carbon contents of the iron compounds.

In order to improve the resistance of grey iron to the corrosive action of the products of combustion as well as to the internal stresses arising from the heating, haematite mixtures are used with great success. As a rule, about 30 per cent of this material should be added to the grey iron mixture to obtain the best results.

Another important point is to take the melting pot into service without attempting to improve its appearance by cutting or grinding off unsightly spots or crusts. The pouring skin is the most effective protection of melting pots against the corrosive action of the firing gases as well as the metal. Indeed, an undamaged natural pouring skin represents 50 per cent of the total life of the pots. Once broken, the underlying metal will be attacked rapidly, particularly by hot zinc, and local corrosion will proceed until the pot begins to leak.

By far the best results have been attained with melting pots made of steel, or semi-steel, which, under ordinary melting conditions will last two or three times as long as good quality grey iron pots.

Steel has proved to be particularly advantageous as material for melting pots used for the refining of lead or for producing remelted or guaranteed zinc. While in producing refined lead, 10-ton grey iron pots will last about 45 to 60 charges, steel pots will—with reasonable treatment—stand at least 100 to 125 charges before showing signs of weakness. The same is true of the relative endurance of grey iron and steel melting pots for the melting of zinc. While remelted

scrap zinc will ruin any grey iron pot within two or three months, steel pots will last half a year or more, operating 24 hours daily.

Instead of straight steel compositions, semi-steel is frequently used for the production of high-grade melting pots. Opinions concerning the relative value of steel and semi-steel pots are by no means uniform, but it appears that the striking inferiority of one or the other material reported by different users is due more to the individual treatments accorded than to real inherent differences in the respective suitabilities of steel and semi-steel pots. A number of American metal works have used semi-steel pots for years at a time without experiencing the least amount of trouble, while others preferred to switch over to steel pots, or even to return to the use of ordinary cast iron pots. The author has found that for ordinary white metal melting, steel pots as well as semi-steel pots will last a number of years, while for remelted zinc, both types of melting pots stand up much longer than grey iron melting pots.

Apart from zinc, aluminum and its alloys possess a strongly corrosive action on iron materials, and considerable experimental work has been carried out to develop melting pot materials of sufficiently high resistance to the corrosive influences of these metals. It must be remembered that the deteriorating action of aluminum on iron melting pots is due not only to the purely chemical action of this metal, but to the extraordinarily high temperatures of the aluminum process as well. Thus, while as a matter of practical experience ordinary grey iron pots are more resistant to the chemical action of aluminum, steel is doubtlessly better suited to withstand the mechanical and chemical action of elevated temperatures. It is possible that semi-steel pots offer a satisfactory solution of this problem, but nothing definite has been published on this subject.

The rim of all melting pots must be made strong and wide enough to safely carry the filled pots. Where the capacity of pots exceed 7 to 8 tons, a second supporting flange should be provided midway between rim and bottom of the pot (see Figure 9).

The rim of the pots is supported on a heavy cast iron plate covering the entire surface of the furnace and preventing gradual destruction of the brickwork by the working tools as well as the penetration of spilled metal into the masonry. The lower supporting flange of the larger types of melting pots rests upon a heavy cast iron ring lying within the upper flue channel leading around the pot. While most of the top plates are made in one piece, they are frequently

cast in two sections cut diagonally and bolted together so as to leave enough space for the expansion of the melting pot. As a rule, $\frac{1}{2}$ to 1 in. is allowed for expansion, the exact figures depending upon the size of the pots.

Melting Pot Hoods.—All melting pots should be supplied with sheet iron hoods, which serve to take up and remove metallic fumes and dust, and to prevent serious accidents. The flue of the hood should be made telescopic so as to permit raising and lowering. Accurately balanced counterweights serve to take care of the changing weights of the hood.

The hood must be made large enough to take up a certain volume of fumes previous to their escape into the flue. As a rule, they are constructed entirely too small to serve their purpose, particularly in the case of remelted zinc plants, which should be supplied with exceptionally high hoods (Figure 39). The same applies to the flues which must be wide enough to take care of all the fumes and steam generated. This fact, while readily recognized everywhere, is rarely considered in building the hood, and practically all the fume trouble in white metal smelters is due to this oversight.

There is another factor of importance to be considered in the construction of hoods, which if ignored will give rise to considerable difficulties in their operation. The inside diameter of the hoods should conform to that of the melting pot (Figure 8). If larger, the splashing of the worked and boiled metal will soon cause the formation of a rapidly increasing ring of metal which adheres to the lower part of the hood and raises its weight sufficiently to render it unmanageable, in spite of the counterweights placed at the other end of the hood-raising device.

Construction of the Melting Pot Furnace.—Apart from the design and material of the various melting pots used, the efficiency of plant is chiefly determined by the design of the furnace, a factor which, in spite of its obvious importance, is still a matter of profound dispute among metallurgists.

This is particularly true of the upper part of the furnace, that is to say, the various systems of channels provided for the conduction of the hot firing gases around the walls of the melting pots. It goes without saying that in the case of small melting pot furnaces, holding less than, say, 2000 pounds of white metal, the importance of this consideration is not as serious as with the 10,000 to 20,000 pound

units, and the most reasonable construction in this case is a simple firing arrangement without any flue channels whatever. The melting pot is simply set into the firing and the flue gases are drawn off about 6 inches below the iron plate, preferably at the opposite side of the fire door. The natural draft will then force the gases of combustion to completely surround the walls of the pots, thus providing for practically uniform heating of the pots.

Combustion efficiency does not permit of as simple a solution in the case of larger units, holding from 3000 to 4000 pounds of metal or more. In order to make the most of the calorific value of the fuel, the products of combustion must not be led directly into the flue, but should be made to rotate around the walls of the pot. This effect may be obtained in two ways. The gases may be led around the pots through one or two large horizontal flues, depending upon the size of the units. The other construction provides for a system of small flue channels. While this latter design will give perfectly satisfactory results with gas-fired melting pot furnaces, it should never be applied where solid or liquid fuel is employed, since apart from the mechanical weakness of this construction, the small flue channels are easily clogged up by flue dust and soot, impairing the draft, and decreasing the general heating efficiency of the system. The pot must frequently be raised to clean out the flue channels, and the stress imposed upon the thin edges of the brickwork forming the channels by the raising and lowering of the heavy pots will cause them to crumble rapidly. It is evident, therefore, that the only efficient melting pot furnace construction is that indicated in Figures 8 and 9.

To prevent undue burning of the bottom of melting pots, the distance between bottom and grates should be at least 12 inches if soft coal is employed as fuel. With hard coal or coke, this distance should be increased to at least 15 inches. If gaseous fuels are used, the burners must be placed proportionately deep, and somewhat inclined so as to prevent the tip of the flame from reaching any part of the melting pot. Quite frequently, the gas or oil burners are directed horizontally in such a way as to cause the gases of combustion to rotate within the walls of the furnace, but even in this case, local burning of the walls of the pots may be caused by uneven construction of the masonry. It is clear that any obstruction in the pass of the flames will project an evenly hot tongue of flame against the corresponding point of the pot-walls, and it is absolutely necessary,

therefore, to provide the flue channels of gas and oil fired melting pot furnaces with a smooth and evenly rounded lining of highly refractory material.

Forced draught or secondary air supply should under no condition be employed. The air entering through the fire or ash door of the furnace must suffice for this purpose.

Efficient operation of melting pot units also necessitate the provision of fairly comfortable working conditions. The rim of the melting pots should be situated about 25 to 30 inches above smelter floor. This elevation not only allows the operators to work and ladle-out the metal with comparative ease, but will also render fire box and ash pit easily accessible.

The above figures apply to the common 3 or 4 ton pots only. They are greatly modified by the size and shape of pots as well as by the type of fuel used. The rim of very small melting pots, such as are used for melting small quantities of white metal solder, is often maintained as high as 40 to 45 inches above ground, thus permitting fire box and ash pit to be located above floor level. Very large and deep pots, on the other hand, are most advantageously built somewhat lower in order to facilitate operation of the long-handled ladles.

Where solid fuel is being used, the pit in front of the fire box should be made wide enough to take care of a small supply of fuel and to permit the operator to protect himself against excessive radiation of heat from the fire box. It should also be sufficiently long, to render the use of shovel and other tools fairly comfortable.

Where the space available for this purpose is too confined, the firing and ash pit of the furnace may be transferred to the outside of the building, a mode of construction frequently met with in European residue smelters. Apart from the advantage of providing for sufficient working space, this arrangement possesses the following advantages:

1. Excess heat and dust connected with the operation of the firing is removed from the smelting room proper.

2. Since the melting pot furnaces are built directly against the walls of the building, considerable working space is saved, in addition to that gained by the outside location of the firing pit.

3. Piles of coal, slags, and ashes do not take up valuable floor space, and the room atmosphere is freed from the dust occasioned by their handling.

The outside working pits should be covered by a roof, of course,

to protect the operators against the inclemency of the weather, while much time is saved if doors are provided near the furnaces, unless the fires are operated by an extra help outside the building.

Fuel.—Owing to the sensitiveness of the bottoms of melting pots to the corrosive influence of the hot gases, some consideration should be paid to the choice of the right kind of fuel, the most harmless in this respect being lignite, the soft and even heat of which make it an ideal fuel from a purely thermo-technical point of view. Unless a strong old lignite, or a soft black coal is used, it should be briquetted in order to avoid too much loss by dusting and falling through the grate, and to prevent a too rapid clogging-up of the flue channels.

The most important disadvantage connected with the use of this fuel is the rapid consumption of even deep layers of lignite or soft black coal, thus necessitating constant observation of the firing. In view of the comparatively deep layers of fuel required, the draft must be proportionally strong, while with insufficient air supply large quantities of heavy black smoke and soot are produced. Another consideration is the low calorific value and the high percentage of ashes produced. The percentage of fine coal dropping through the grates also is a significant factor of economic importance.

Long flaming channel coal is doubtlessly best suited for melting pot furnaces, since the advantages offered by its soft, even, but comparatively hot flame are not accompanied by the disadvantages associated with the use of lignite or similar fuel.

Short flaming furnace coal may also be used. While the flame is slightly cutting, it will not appreciably hurt melting pots of fairly good composition, while the disadvantages above indicated are still further reduced.

From the foregoing, it may be concluded that the use of coke is not conducive to the longevity of melting pots. However, the author has seen quite a number of white metal plants where gas coke is exclusively used for this purpose. The fact that the combustion period of coke is much longer than that of other solid fuels, serves not only to facilitate the work of the operators, but is claimed to afford considerable financial savings. While the corrosive tendencies of the coke flame cannot be denied, of course, they may be combated successfully by rotating the melting pot around its vertical axis as frequently as possible, and by increasing the usual distance between the bottom of the pots and the grates to about 15 inches. Filling the ash pit with water cannot be recommended with coke firing, of

course, since the hydrogen formed by the conversion of water vapors within the hot coke bed will increase the cutting propensities of the coke flame to an excessive degree.

Oil should under no condition be burned in melting pot furnaces, since it is practically impossible to regulate the oil flame so as to produce a sufficiently soft flame without killing it in the attempt, or without wasting a disproportionally large amount of oil.

There cannot, however, be any serious objection to the use of gas if the burners are so regulated as to prevent the tip of the flame from touching the bottom or the walls of the pots. In order to soften the flames somewhat, less primary air should be used, the final combustion being left to secondary air entering through the furnace door.

Treatment and Care of Melting Pots.—The longevity of melting pots is governed to a surprising degree by the care bestowed upon them before placing them into service and throughout smelting operations, and by the attention paid to the different points of danger peculiar to this type of melting appliance. The best of melting pots, built in according to all established scientific principles, may be ruined within a few weeks by inefficient and careless treatment. It is significant, indeed, that all those smelters, paying small attention to the shape and quality of the various types of pots used, are most careless in their treatment of the pots before and after taking them into service. This state of affairs would be quickly eliminated if smelter officials would realize that the actual expenses of the pots represent only one of the various sources of loss caused by frequent changing of melting pots, accompanied as it is by an often serious loss of metal by leakage before the failure of the pot is discovered, and by a considerable waste of time occasioned by the change of pots.

Where a stock of melting pots of various sizes is kept on hand, they should be treated with care from the time they are received at the smelter. If possible, the pots should be stored in a thoroughly dry place, protected against rain or moisture. If dry space is not available for this purpose—and it is hard to imagine that with a little effort this should be the case at any plant—the pots should be placed upside down on a hard, somewhat inclined surface, thus avoiding the formation of pools of water under the pots. In any case, however, all pots reaching the plant should be provided with an inside and outside coating of tar, which protects the iron or steel against the direct influence of water or moisture, and which is easily chipped and burned off on taking the pots into service.

It has been stated above that the longevity of melting pots depends to a large degree upon the soundness of the pouring skin. Since on account of its considerable contamination with iron oxide and other impurities this skin is particularly subject to electrolytic action, its partial destruction by water is a matter of a comparatively short time only, while the corresponding shortening of the life of melting pots is disproportionally severe.

Empty pots should not be exposed to high heat in order to avoid considerable internal strains, which tend to weaken the structure of the iron or steel towards mechanical and chemical influences. In starting up a pot, a small fire should be maintained and increased but gradually as the pot fills up with metal. Few pots will stand repeated and prolonged heating while empty, without cracking sooner or later. It is an almost daily occurrence in the majority of residue smelters, working in day shifts only, to have the night watchman heat up the pots during the early morning hours so as to have them "nice and hot" at the start of the morning shift. It is quite true, of course, that the working speed of the plant is considerably accelerated by this arrangement, but the same result may be achieved in a more efficient way if the second day shift melts a few hundred pounds of metal in the pots, filling them up with ingots or scrap before leaving. If, then, the pots are heated up in the early morning, the gradually increasing heat will remelt the solid layer of metal in the bottom of the pot and, later on, the cold ingot or scrap charge without damaging the pots.

Highly heated streams of metal should not be permitted to bear down upon the unprotected bottom of the pot, since both the effect of the internal stress set up by the excessive local heating as well as the corrosive and erosive action of the hot metal will, within a short time, disable the melting pot for further use. This is particularly true of pots acting as forehearths to reverberatory furnaces. If the bottom of the pot is not covered by a sufficiently deep layer of metal, a strong and sufficiently large piece of sheet iron should be placed within to take up the first blow of the stream.

Heavy slabs or bars of metal must not be thrown into the pot from full height. Deep vessels, particularly, may in this way be damaged very easily, especially if red hot. The bars of metal should be made to slide down the side of the pot.

In order to avoid contamination of consecutive charges of different alloys, as well as to protect the pots against corrosion, they

must be cleaned thoroughly as often as possible. Nothing less than a good strong steel brush will do for this purpose. The cleaned pot should then be given a heavy washing with a thick emulsion of lime or, better, a mixture of lime and graphite. The fine lime and graphite particles will enter all the pores and fissures of the iron walls, and protect them against the corrosive action of the hot metals and of the substances employed to refine them.

Every stationary iron or steel melting pot exposed to a stationary source of heat will always exhibit one certain spot at the bottom or the lower parts of the walls suffering in a particularly high degree from the influence of the heat. This is specially true of the pots heated with gas or oil, and most pots that have to be taken out of service are found to have been weakened or perforated in one place only, while the rest of the bottom and walls shows very little wear, if any. The two most exposed parts of a melting pot are (1) the point where the draught directs the heat-center of the flames against the front section of the bottom, or wherever the tip of gas or oil flames touch the bottom or walls, and (2) the place where the fire gases enter the connecting flue channel leading to the horizontal channels encircling the pots.

To prevent this concentrated attack on isolated sections of bottom and walls of melting pots, the pots should at certain short intervals be rotated around their vertical axis far enough to expose other parts to the action of the heat centers. If possible, this should be done at least once a week, moving the pot around about 5 inches each time.

Melting pots of the type represented by Figure 10 cannot, of course, be rotated, the only means of preventing their premature perforation being the strengthening of the most exposed parts and the choice of soft burning fuel. Care should be taken, however, to guard against abrupt changes of thickness.

CHAPTER XXII

PRECIPITATION AND RECOVERY OF FLUE DUST

Flue channels and flue dust collecting devices are designed to accomplish two chief purposes:

1. To serve as connecting link between furnace and chimney for the supply of sufficient draught to obtain the furnace temperatures and, eventually, the oxidizing atmospheres required.

2. To aid in the precipitation of flue dust and metallic vapors, thus regaining a considerable percentage of the metal lost by dusting and volatilization, and preventing too large a contamination of the chimney smoke with metallic vapors obnoxious to neighboring homes and establishments, which often form the subject of expensive law suits.

While with efficiently constructed flue channel systems it is possible to effect extensive condensation and precipitation of metallic vapors and flue dust produced in metallurgical residue smelting operations, several types of vapors such as certain forms of zinc oxide vapor defy any attempt at precipitation by simple mechanical means, and if these are produced in large quantities, special condensation and dust collecting devices must be installed, most suitable for this purpose being bag filter and electrolytic condensation plants.

Non-metallic vapors such as ammonia, hydrochloric or sulphuric acid vapors, etc., also are very difficultly condensed, but this question is of comparatively small importance to the average residue smelting plant. Wherever large quantities of chemical residues are handled and correspondingly large volumes of acid vapors are to be taken care of, only the installation of a gas-washing apparatus or of an electrolytic condensing plant will render satisfactory results, unless the gases or vapors are of such a nature that the introduction of alkaline or acid substances, such as powdered lime, into the flue channels leads to the production of a compound easily precipitated. However, since in most instances the quality of the flue dust is in no way benefited by contamination with large quantities of chemical compounds, the latter process is of local importance only.

The most important of the recoverable substances are: the oxides and sulphides of practically all metals, excepting some forms of zinc oxide, the vapors of practically all important metals and metalloids such as tin, lead, antimony, arsenic, mercury, and sulphur, as well as components of slag forming additions of the furnace charges such as iron oxide, lime, etc.

The precipitation effect exerted by the various devices employed is chiefly governed by the nature and the contents of the flue gases, the qualitative and quantitative drawing capacity of the chimney or stack, and by the correct application of the various principles underlying condensation and precipitation. Since it is economically impossible for many of the smaller plants to install complicated collection devices or, even, to improve the chimney capacity by installing efficient machinery, it is necessary to exhaust every possibility offered by the natural means of condensation and precipitation and to avoid the numerous constructional errors easily introduced by ignorance of the various principles in question, or by negligence in their application. The application of any of the dust precipitating devices requires the provision of sufficient draught. The chimney capacity must be large enough to take care of a given volume of flue gas and to permit of the application of one or more of the various natural principles of condensation and precipitation. The larger the drawing capacity of the chimney, the greater the draught reserves available for the installation of common and inexpensive systems of precipitation. Since the operation of more complicated condensing and collecting devices, such as bag filters or electric condensers, requires the use of artificial draught in any case, this consideration is not quite as important, but it is obvious that even in this case the efficiency of the system is greatly improved if the energy of the exhaustors is expended only in overcoming the additional resistance exerted by the artificial dust collecting devices.

Cooling of the flue gases, one of the most important factors in the precipitation of flue dust, especially with flue gases of very high temperatures, may be effected by installing cooling chambers provided with sufficiently thin walls to permit of a high degree of radiation. A certain cooling effect is also obtained by passing the gases through long flues situated above ground, particularly if one or two sheet iron chambers are inserted in the flue system.

Direct air cooling of the flue gases is usually effected by introducing cold outside air through a series of tubes or slits penetrating

the roof of the flue or chamber, but this method is not, as a rule, applied under ordinary conditions, since the introduction of cold air into the flue system imposes too much of a strain on the drawing capacity of the chimney. Similar, or better, results may easily be obtained by other methods without incurring as serious a loss of draught. Only, where indirect cooling by air or other agencies cannot be applied, and where a sufficiently large excess of draught power is available at all times, may cold air be introduced into the flue channels. The introduction of a stream of preheated air in order to cause the formation of vortices without causing a corresponding increase of the density of the flue gases—a method proposed by one or two European writers—is thoroughly impractical since vortices may be induced in a number of ways without adding to the volume of gas handled by the chimney.

The induction of vortices within the gas currents is one of the most effective but also the most troublesome methods of dust settling, and it is a common experience among the smaller type of residue smelting plants that no pains are spared to avoid even the accidental formation of vortices, a fact exclusively due to the always very meager excess of draught power available. Vortices may be produced by:

1. Breaks in the flue channels,
2. Introduction of thin streams of air into the channels,
3. Local reduction or expansion of the cross-section of flue channels,
4. Suspension of wires or baffle plates in the channels,
5. Injection of water vapor or spray,
6. Rough and uneven surfaces of the walls of channels.

Of these factors, the first may be eliminated without further discussion since the loss of velocity incurred is too serious to justify its application. Much better results are attained with a large number of small vortices such as are induced by thin streams of water vapor, spray, suspended wire, etc.

The effect of thin streams of air on the settlement of dust has been discussed.

Local reduction and expansion of the cross-section of flue channels represents two of the most important simple dust settling devices, especially since they are of comparatively small influence on the drawing capacity of the chimney. It is evident, of course, that even they require a certain, although small excess of draught power, but if this

is available, reduction and expansion of the gas current will cause the settling of a considerable percentage of valuable flue dust.

Contraction of the cross-section of flue channels is effected simply by narrowing the walls of the channels down to about one half of the average cross-section of the system at one point. As a rule, this purpose is achieved by building a brick wall across the channel leaving an opening of the required cross-section. For instance, if the flue channel is 3 feet wide and 4 feet high, the opening may be made about 2 by 3 feet. The constriction of the gas current followed by a corresponding degree of expansion will cause a certain quantity of dust to settle out, although the creation of vortices introduces another influential factor.

While the constriction of the gas currents is bound to cause a proportional loss of velocity or drawing capacity, local expansion of the cross-section of the flue channels does not impose any strain upon the draught power of the chimney, and the construction of one or a number of settlement chambers, correctly proportioned, will therefore be of appreciable value in any flue system, no matter how short the channels and how small or large the amount of vapors and flue dust carried by the flue gases.

Settlement chambers are among the oldest dust collecting devices known. It is the most effective of the simple settling arrangements, especially since it lends itself admirably to the application of a number of other devices for the condensation of metallic vapors and the settlement of the dust. The principle of the settling action of the chamber is the following: If a gas current, moving along in a channel 4 feet high and 3 feet wide at a velocity of 15 feet per second, enters a chamber 8 feet wide and 8 feet high, the velocity is reduced to less than 3 feet per second. It is obvious that if the chamber is made long enough, a large percentage of the solid contents of the flue gases will have settled out before the gas current is again contracted to its original cross-section. However, since practically perfect settling of the dust requires a time of flow of approximately 10 seconds, this chamber would have to be about 30 feet long, although by cooling the gases, or by introducing water vapor or spray, etc., the speed of settling could be considerably increased. Where the flue channels pass along the outside of a building, the chamber may be erected above ground, thus increasing the efficiency of the process by lowering the temperature of the flue gases. It is necessary, of course, to guard against too strong a decrease of temperatures which

would seriously interfere with the draught power. However, since the drawing capacity of the chimney is not materially increased by any rise in temperature above 600° Fahr., the average smelter gases, especially if derived from reverberatory furnaces may be subjected to a considerable reduction of temperatures without endangering the efficiency of the chimney.

The settling efficiency of the chambers may be noticeably increased by water vapor or spray injection devices, or by the creation of vortices by means of wires or baffle plates suspended from the roof of the chamber. The relative efficiency of the latter type of dust

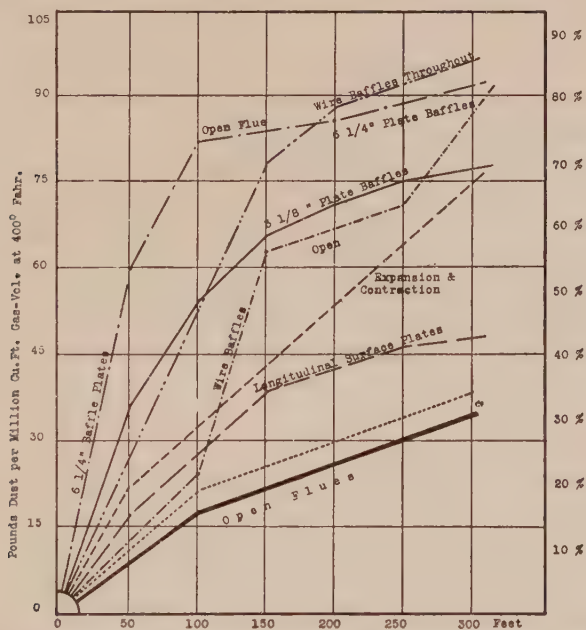


FIG. 58.—EFFICIENCY OF VARIOUS FLUE DUST ARRESTING DEVICES.

arresting devices has been determined experimentally at the Great Falls Copper smelter, the results of these tests being represented graphically in Figure 58.

The diagram shows that the settling effect of the various devices is almost directly proportional to the degree of obstruction offered by the baffling materials. Wide baffle plates suspended in such a way that the gas current strikes the face of the plates are more effective than the narrower types, while the latter precipitate more

dust than other plates hung with axes parallel to the flow of gas. Wire baffles, while not quite as effective as baffle plates suspended against the gas current at shorter distances, are more efficient than any other dust settling device with long dust chambers. The diagram also shows that expansions and contractions of the flue channels represent very efficient dust settling devices, while under the testing conditions which prevailed at the Great Falls Plant, open flues 300 feet long caused the settlement of not more than about 35 per cent of the flue dust carried by the flue gases.

Considering the results of this test from a practical point of view, and applying them to the average conditions obtaining in residue smelting plants, the following deductions are in order:

Supposing the average length of flues to be about 100 feet, and disregarding the effect of larger dust chambers, the settling efficiencies as determined at Great Falls are as follows:

TABLE 42

	Per cent of fall
Open Flues (1).....	18
Open Flues (2).....	20
Longitudinal surface plates.....	27
Expansion and Contraction.....	27
Wire baffles throughout.....	44
3½-in. Plate baffles.....	49
6½-in. Plate baffles.....	72

In view of the obstruction to the flow of the gas currents and the corresponding loss of draught capacity caused by larger and smaller transverse plate baffles, these are of no practical interest here, unless there is no objection to the construction of large flues and to the installation of artificial draught machines. The suspension of baffle plates with axes parallel to the flow of gases, while less obstructive to the flow of gases, does not offer any marked advantages, since a much higher degree of settling efficiency is obtained with wire baffles, which are much easier and more cheaply installed than plates. The only practical advantage of longitudinal surface plates over wire baffles is that in contrast to the latter the adhering dust need not be shaken off, the layer of dust dropping off automatically as soon as a certain maximum thickness is reached. Baffle wires must be shaken at least once or twice a day.

Since it is practically impossible, of course, to shake each wire

individually, they must be suspended from wire netting fixed on frames. For this reason, and in order to improve the settling efficiency by decreasing the velocity of the flue gases, the wires should be hung in dust chambers large enough to accommodate several thousand wires. These chambers are most conveniently built above ground and arranged as shown in Figure 59, which represents a settlement chamber built by the author for a South German residue smelting plant. The efficiency of this chamber, which is subdivided into five divisions, 15 feet long, 4 feet wide, and 7 feet high, is very high, the percentage of precipitated flue dust often amounting to as high as 40 per cent. The considerable loss of draught power caused by this arrangement necessitated the installation of a five-horsepower exhaustor.

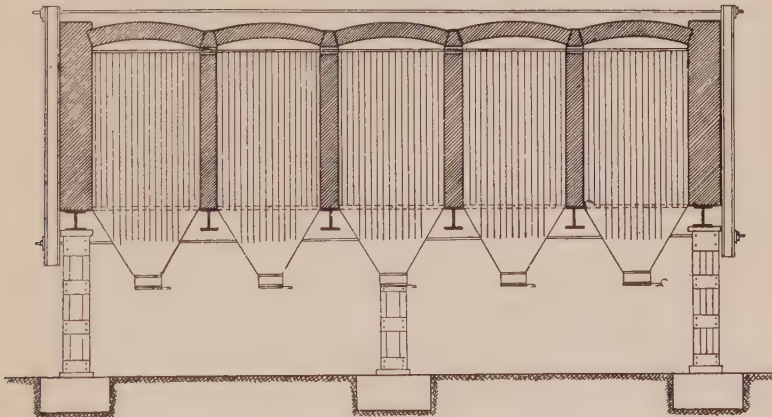


FIG. 59.—SETTLEMENT CHAMBER WITH WIRE BAFFLES.

Figure 59 shows the wires to be suspended from long iron rods fastened on both sides to horizontal flats. A thin steel rope is attached to each end of the flats which is passed over a concave rimmed wheel attached to a stout support about 12 inches above the flats. The other end of the rope is provided with a ring or handle, so that by pulling the rope, the flats holding the ends of the rods are lifted about 2 inches and dropped again, the shock transmitted to the wires loosening and dislodging the adhering layer of dust. The hangers are laid about 4 inches apart, the total number of hangers in the construction shown in Figure 59 amounting to 45, at a maximum number of wires of 3200.

Not quite as effective under ordinary conditions, but much more simple and inexpensive than plate or wire baffles is the injection of steam or water spray into the dust chambers, provided the installation conforms to the various principles underlying the use of these dust settling devices. Of greatest influence on the efficiency of these systems is the location of the jets and the direction of the spray relative to the direction of flow of the gas currents. Where the water spray is to be introduced into a chamber located somewhere along a flue channel the only logical position of the spray is at the entrance side, that is to say, at the upper right- or left-hand corner above the flue opening, the spray being directed diagonally across the chamber, in the direction of the current.

The precipitating effect of the water or vapor spray is based upon the fact that the small drops making up the mist attach themselves to the particles of dust, increasing their weight and facilitating settling. If part of the metallic contents of the flue gases are present in the gaseous form, the water vapor or the fine mist of water produced by the nozzle cause their condensation in the same manner that great clouds of dust such as are thrown out by active volcanoes will produce heavy rains. The small particles of solid matter thus produced are immediately loaded with a tiny drop of water infinitely heavier than the particles themselves and are thus precipitated much more readily. It is clear that for this reason the nozzle must be located where the flue gases enter the chamber so as to permit the mist, or vapor, to exert its settling effect under most favorable conditions for as long a distance as possible. While, relatively speaking, the influence of the water on the flue dust, or fumes, will still be effective after the gas has re-entered the channel, it is obvious that in view of the greatly increased velocity of the gas currents the settling effect must of necessity be considerably weaker.

Filtration of gases is now exclusively carried out by means of bag filters, woolen or cotton cloth bags being in general use. While the woolen bags are preferable to cotton, resisting heat and corrosive gases better than the latter, both materials are being used in great numbers. For ordinary residue smelting work the cheaper cotton bags will be found to operate just as efficiently as the woolen grades. The principle of bag filtration is indicated by Figures 60 and 61.

The gases are delivered at the bottom of the cylinders, representing a unit, and containing from 1 to 12 filter bags, through which

they are pressed or drawn at a velocity of from 4 to 6 feet per second (measured in the dust chamber), about 2 cubic feet of fumes per minute per square foot of bag surface being considered the capacity of bag cloth with 24 threads per inch in warp and woof.

The most essential part of the filter bag is the nap on the inside

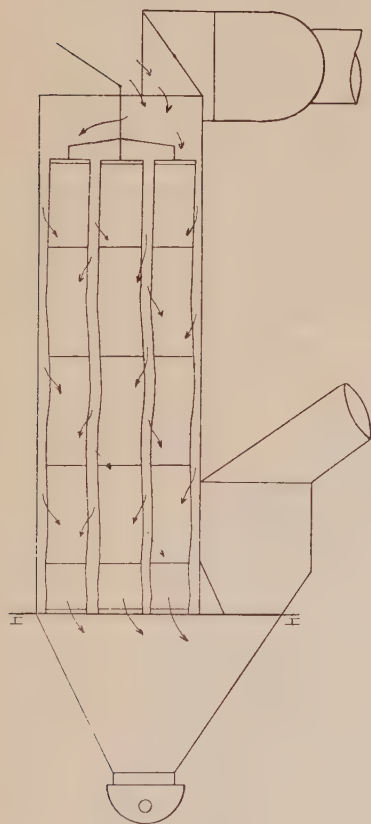


FIG. 60.

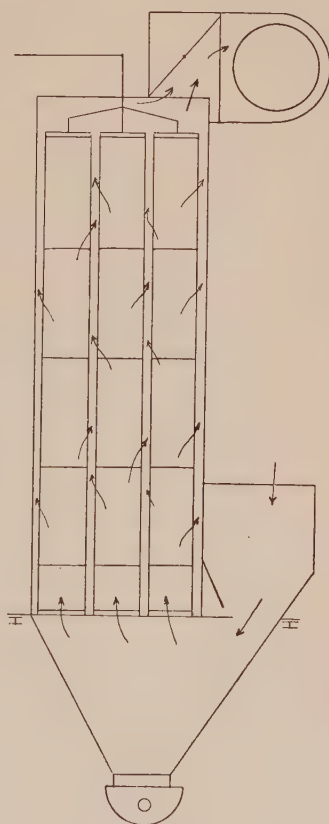


FIG. 61.

FIGS. 60 AND 61.—BAG FILTRATION PLANT.

of the bag, without which the filter cloth becomes pervious to all but coarse flue dust. It is natural that after a certain period of operation the collected dust deposited in the nap becomes too heavy and dense to permit of the passage of fresh gases, so that the bags

must periodically be shaken by hand or mechanical apparatus to remove the accumulated dust which is collected in hoppers installed beneath the bags.

Shaking by hand, while less efficient than mechanical shaking, possesses the advantage that, on account of the lesser strain imposed, the bags last considerably longer. Hand-operated bag filters are shaken at least 5 or 8 times per day, but since the efficiency of the filter bag apparatus is dependent on as unobstructed a passage of the flue gases as possible, more frequent shaking is advisable.

The filter bags in each unit forming one group are suspended from levers. At certain periodical intervals the levers are slightly lowered by mechanically operated cams to be suddenly returned to their old position, an operation which is repeated several times in short order. This sharp jerking motion tends to disengage the bulk of the dust from the filter cloth, but this would immediately be drawn back against the cloth if the air currents were permitted to be sucked or pressed through the filter during shaking. In order to avoid this, and to increase the efficiency of the bag filter plant generally, compressed air is permitted to flow into the cylinder at certain intervals—corresponding to the shaking periods—which causes the reversing gate to shut immediately, cutting off the dust-laden flue gases, and opening the cylinder to the outside air. A strong counter current, penetrating the filter bags from the outside, is thus produced, which removes all dust and fume particles from the nap and forces the deposits out of the bags and into the hoppers. The closing and re-opening of the reversing gate is so timed as to take place a few seconds before and after the shaking operation, thus permitting the dust particles to drop into the hoppers before the upward motion of the air, or flue gases, is resumed.

This reversal of the air current offers the additional advantage of forcing the thin fibers of the nap, which are gradually pressed against the cloth, seriously obstructing the passage of the flue gases, back into their original position.

The number of shakings per unit of time depends upon the specific capacity of the filter bag plant and on the nature of the dust and fumes contained in the flue gases. With modern mechanical apparatus it is possible to adjust the shaking periods so that the 4-second periods may occur once within from 3 to 120 minutes. It is self-evident that the periodical entrance of fresh air into the bag cylinders causes a slight reduction of drawing effect, but this loss may easily

be disregarded, even if the shaking periods recur every 4 or 5 minutes.

In view of the organic nature of the filter bags the temperature of the flue gases entering the baghouses must be regulated accordingly. Where the distance between furnace and baghouse is too small to cause natural cooling below the critical temperature, artificial cooling must be resorted to. Best results are obtained, of course, if the cooling process is carried out so as to effect the settling of a large part of the flue dust. Some of the larger smelters have installed steel cooling pipes, while others, particularly in Europe, pass the hot gases through large dust chambers built of sheet iron above ground.

In considering the permissible maximum temperatures of flue gases in filter bags, attention is called to the fact, that the critical point is not determined by the flaming temperature, but by the decrease of the strength of the filter cloth, to which both woolen and cotton filter bags are subjected at comparatively low temperatures. H. H. Alexander¹ carried out comprehensive experiments to determine the influence of various temperatures, applied for different periods of time, on woolen and cotton bags, obtaining the results indicated in Table 43 on next page.

Another difficulty occasionally encountered in residue smelting plants is the burning of filter bags caused by a subsequent final oxidation of hot metallic suboxides, such as the lower oxide of zinc, or what is known as such, but which most probably represents a mixture of zinc oxide and metallic zinc fumes. If brass alloys, or other materials high in zinc are smelted in blast furnaces, and the process is carried out so as to avoid top fire, the settled flue dust shows a tendency after a short time to grow hot, producing considerable fumes and often turning red from heat. This phenomenon is doubtlessly due to a final oxidation, and it is obvious that under the conditions obtaining in the filter bag during operation, that is to say, under the combined influence of elevated temperatures and draught, spontaneous oxidation of the zinc-zinc oxide dust deposits are practically unavoidable. The only practical way of preventing the more or less frequent destruction of entire sets of filter bags is to maintain a top fire, which offers sufficient security against the presence of inoxidized or partly oxidized zinc in the flue dust.

Washing the flue gases with water or chemicals is rarely practiced

¹Trans. A. I. M. E., XLIX, p. 561.

TABLE 43.—PERCENTAGE OF STRENGTH LOSS

Cotton

Degrees F.	Time in testing oven, hours				
	1	24	48	96	144
210		0.00			0.00
215		0.00	0.9	6.1	9.40
220		4.20			
225		5.25			
230		7.30			
235		12.10			
240		17.10			
245		20.70			
260	0.3				
265	3.5				
270	5.3				
280	9.6				
<i>Wool</i>					
270		0.00	0.00	0.0	0.0
275				0.3	3.2
280			0.0	5.3	6.9
285			0.0		
290		0.00	2.8		
295		4.0			
300		10.7			
355	0.0				
365	0.0				
370	2.3				
375	4.4				
385	6.7				

in residue smelting operations. Of the various methods suggested for this purpose the following are the most important:

- (a) Forcing the gases through tanks filled with water.
- (b) Conducting the gases through towers provided with sets of inclined shelves, where they are met by jets or sheets of water.
- (c) Washing the flue gases in centrifugal separators.

One of the representative types of centrifugal gas scrubbers is the "Gyro" Air and Gas Scrubber shown in Figures 62 and 63.

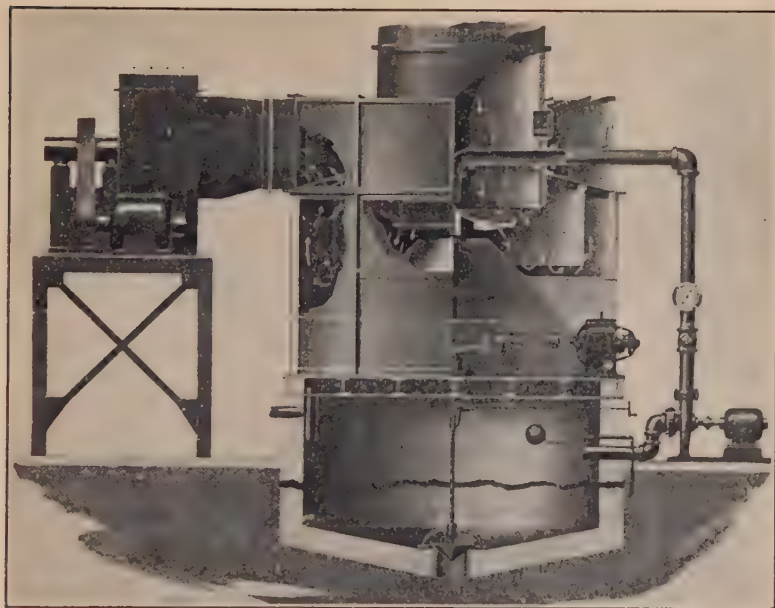


FIG. 62.

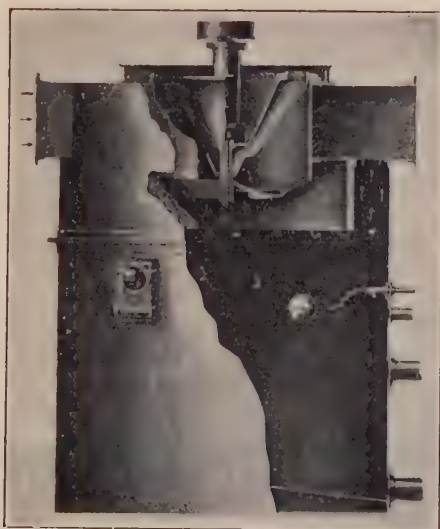


FIG. 63.

FIGS. 62 AND 63.—AIR AND GAS SCRUBBER.

Figure 62 shows a sectional elevation of the Gyro scrubber as designed to handle hot gases up to 1700° Fahr. Scrubbers for colder gases are simpler in construction, since the bearings and motor need no protection from high temperatures. The identical scrubbing principle obtains, however, in either case.

The gases enter the scrubber through the central refractory lined drum at the top and pass through the Gyro wheel. This wheel is conical in shape and has one, two or three concentric rows of pins. The water enters upon the cone at low pressure and is thrown by the centrifugal force of the rapidly revolving wheel against and along the first set of pins. This is repeated against each successive ring, the final ring throwing the water with the entrained solid matter against a splash plate or large drum which is hung at some little distance from the wheel. Thus, the dust entrained in the gases is given an impact, causing thorough wetting of each particle, and forcing the dust to pass off with the water instead of continuing through the wheel in a dry or semi-saturated condition. The gases, in passing through the Gyro wheel, are carried by the water against each set of pins and finally against the splash plate, so that the dust particles receive several hard blows as they are carried against the metal at high velocity.

The gases after passing through the wheel are carried under and around the splash plate and into the bustle pipe which almost completely surrounds the washing chamber, from which pipe it is discharged into the atmosphere.

The water with its entrained solid matter drains down the conical drum into discharge ducts, from which it flows to settling tanks.

The *Electrolytic (Cottrell) Process* represents the process of separating flue dust and fumes by the silent or glow discharge from high-voltage direct currents, which is passed from discharge-electrodes through an air-space to collecting-electrodes. The suspended particles of flue dust and fume, passing upward between the electrodes, take over the electric charges from the ions flowing toward the collecting-electrodes, becoming sufficiently charged themselves to move under the force of the electric field. Alternating current, usually taken from a commercial line, is employed as the source of electricity, which is transformed to the desired voltage, ranging from 15,000 to 50,000 volts, and then changed into an intermittent direct current.

Electric precipitation presumes a certain degree of electric con-

ductivity of the gas, and if the flue gases do not carry sufficient amounts of sulphuric acid anhydride or moisture to render them conductive, a small water injector should be installed to provide for the necessary moisture.

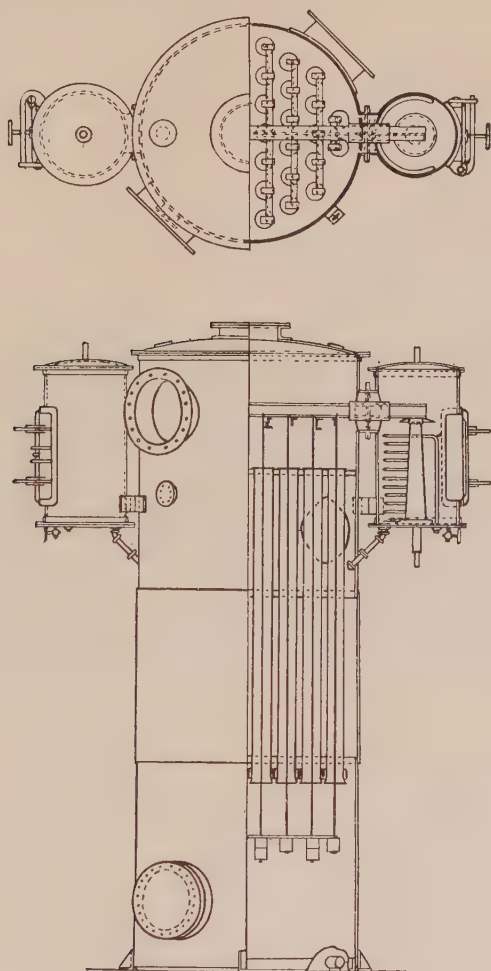


FIG. 64.—PIPE TYPE ELECTROLYTIC PRECIPITATOR.

The precipitating chamber proper consists of a vertical cast-iron pipe, 5 inches in diameter and about 10 feet long, the walls of the pipe serving as precipitating electrodes. Through the center of the pipe a steel wire is drawn which is connected with an intermittent

direct current of the voltage required, and which serves as discharge electrode, or anode. A unit consists of from 300 to 400 of these pipes.

Figure 64 shows a typical pipe type precipitator, while Figure 65 illustrates an assembly of three precipitators, showing details of construction.

The flue gases, cooled to a temperature of about 212° Fahr., are passed through a collecting flue large and long enough to precipitate the coarse dust, ascending through the depositing pipes into collecting pipes, and from there into the main flue or directly into the chimney. All the dust, fume, and moisture is deposited within the pipes. The bulk of the deposit drops off as soon as a certain thickness is reached, while the rest is loosened by knockers, which also serve the discharge-

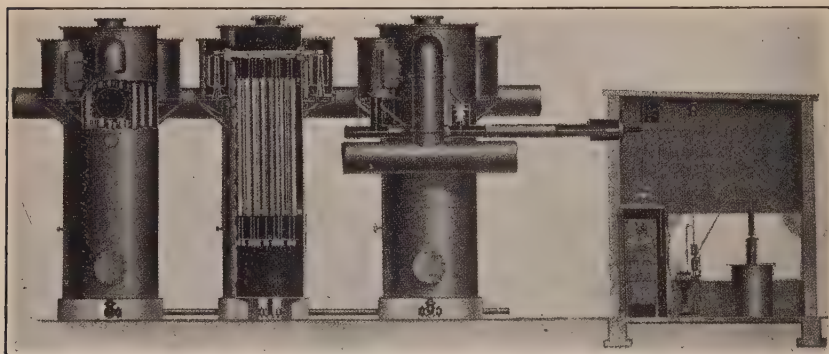


FIG. 65.—ASSEMBLED COTTRELL PRECIPITATING PLANT.

wires to detach adhering layers of fume. The deposits drop into the lower gas chambers, provided with hoppers.

It is obvious that in view of the bulkiness and costliness of a Cottrell plant, this type of dust precipitating device is not suited for any but the very largest scrap and residue smelting works, but even in their case it appears, that practically similar results may be attained with the much cheaper filtering devices, which, besides being less expensive in construction and operation, are incomparably simpler and practically fool-proof. Repairs are easily and cheaply made, and the metallic values are recovered almost as completely as with Cottrell precipitators.

General Considerations.—Since apart from the settling effect of the various natural and artificial settling devices, the amount of flue

dust precipitated is governed by the length of the flues, every smelter operating blast or reverberatory furnaces, or other high temperature units, should be provided with one or more flues of as great a length as possible under existing conditions. A space of 50 or 60 feet long should always be available for this purpose, while lack of space may be made up by correspondingly larger cross-section of the flues. Where the space available does not permit of the construction of a straight flue of sufficient length, one or two bends may be provided, although the angle of these bends must be maintained at 120° or

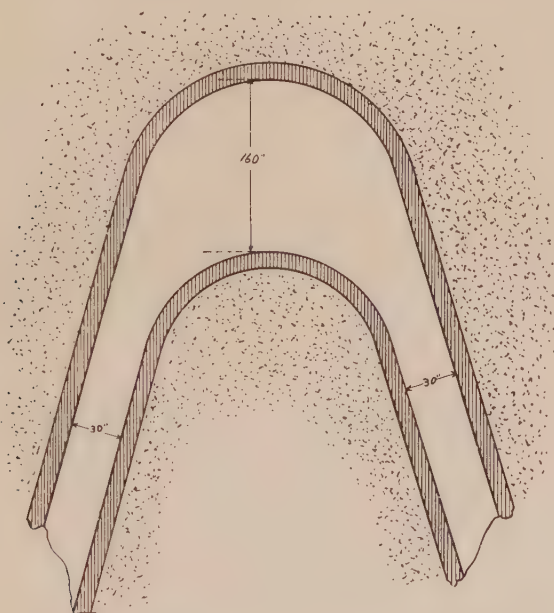


FIG. 66.—CONSTRUCTION OF FLUE CHANNEL BENDS.

larger. Changes of direction must be rounded off, the radii of the bends being maintained as large as possible. If, under exceptionally unfavorable space conditions, sharp angles cannot be avoided, the bends should be converted into dust chambers of sufficiently large dimensions to reduce the loss of draft by friction and the creation of vortices to a minimum. These chambers should be constructed as shown in Figure 66, thus making sure of as unobstructed a flow of flue gases as possible.

Where a number of high temperature furnaces are in continuous

operation and large amounts of different types of flue dust are produced it is good policy to provide for a number of flues, the individual flues serving furnaces smelting only the same groups of alloys or metals. Thus white metal and alloys melting and smelting furnaces should not be connected to the same flues with copper or copper alloy furnaces, while furnaces reserved for the melting and remelting of brasses, and producing large quantities of zinc fumes, should also have an individual flue.

If for financial reasons, or for lack of space, individual flues cannot be constructed, it is advisable to interpose a flue dust chamber between the high temperature furnaces and the common flue, introducing the flue gases through the roof of the chamber, and providing for as long a traveling distance through the chamber as possible by situating the exit opening at the remotest point, a few inches above

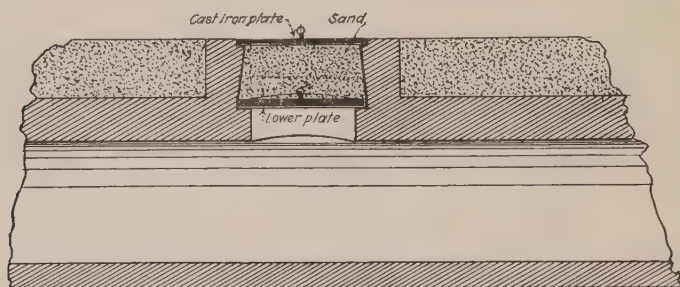


FIG. 67.—FLUE CHANNEL MAN-HOLE.

the bottom. By locating the exit opening level with the bottom of the dust chamber, the dust accumulated there may be drawn out with the gas current.

While the separation of the various kinds of flue dust is not as perfect as may be obtained with separate flues, the latter arrangement will prevent a general mixture of all the flue dust produced, concentrating a large part of the different dusts within their respective chambers. If several flues are to enter a common chimney, it is advisable to run all the flues into a chamber, connecting the chamber with the chimney by a larger flue. The individual flues should not enter the common chamber from all directions, but from one side only, in order to avoid loss of draught by the creation of numerous strong vortices within the chamber.

Parallel running flues should not be connected by open horizontal

manholes, which are bound to create strong cross-currents and vortices, particularly if, on account of differing cross-sections and temperatures, velocities of the gas currents differ in neighboring flues.

In order to facilitate cleaning of the flues and removal of dust, man-holes should be provided at convenient points not too far removed from each other. Figure 67 indicates the most efficient simple construction of these openings.

If the flue system contains a number of dust chambers, the man-holes are most conveniently located in the roof of these chambers.

CHAPTER XXIII

TREATMENT OF FLUE DUST AND FUMES

Efficient treatment of flue dust and fumes is one of the most difficult problems continually facing the residue smelter. It is well known that if flue dust in its original loose condition is charged back into the reverberatory furnace, more than half of the total quantity is often carried over into the flues, but similarly bad results are also obtained if the flue dust is simply wetted down and charged, alone or mixed with other raw materials, since immediately after drying a large percentage of the flue dust is blown out again.

There are a number of soluble salts which if present in wet flue dust, prevent undue dusting of flue dust in reverberatory furnaces. The most important of these is zinc sulphate, and if wet flue dust containing about 2 per cent of this compound is left to heat up quietly in a reverberatory furnace until the fusion point is reached, loss by dusting is reduced to a minimum. A few per cent of ferrous sulphate in wet or wetted dust also tends to eliminate excessive dusting, although in either case, the full binding property of these substances is only brought out by forming the wet flue dust into small shapes suitable for reverberatory melting and depositing the "briquets" in a dry and warm place for a few days.

Flue dust may be compacted by the following methods:

1. Briquetting by hand, for reverberatory smelting,
2. Briquetting in mold presses, for blast furnace smelting,
3. Agglomerating by mixing the dry flue dust with molten slag,
4. Sintering in sintering pots, or in continuous type sintering machines,
5. Nodulizing.

For the type of flue dust generally handled in residue smelting plants, briquetting by hand or in mold presses appears to be the only practically important methods of preliminary treatment, especially if only the flue dust and fumes produced by the smelters themselves are being treated.

Briquetting Mixtures.—In making up briquetting mixtures, attention should be paid to the correct choice of binders as well as to the efficient compounding of the various metallic raw materials contained in the different lots of briquets produced. It is quite customary, for instance, to add various types of finely powdered ashes such as type ashes, solder ashes, etc., to the flue dust and fumes, while in some instances, slag forming materials other than lime may be added together with the straight bonding substances.

Many residue smelting plants produce dry and wet flue dust, the latter frequently in the nature of slimes; it is important, of course, to combine both grades in such a way as to cause the least amount of dusting without using more bonding material than necessary. In some instances chemically active substances should be added to the briquetting mixtures with a view to counteracting certain deteriorating effects exerted by some component of the flue dust on the briquetting properties of the mixtures or on the chemical or mechanical properties of the metals or alloys produced. Thus, if considerable amounts of sulphur or arsenic are contained in the flue dust, addition of a little soda ash, or, caustic soda, will cause all of the sulphur and the bulk of the arsenic to go into the slag. Where large amounts of iron filings are available, a small percentage added to white metal flue dust will tend also to eliminate the bulk of any arsenic present in the dust. It is self-evident, of course, that iron filings should under no circumstances be added to straight copper alloy dust, while if—as is usually the case—white metal dust and the flue dust and fumes produced in copper alloy smelting are collected in the same flues, iron filings and sulphide material may be present in the briquetting mixtures to assist in the formation of copper matte.

Bonding Materials.—Of the various bonding materials suggested and used, lime and certain special mixtures composed chiefly of lime are practically exclusively used in the residue smelting industries. It is probably true that a number of other bonding materials such as zinc sulphate possess a more pronounced bonding effect at lower temperatures, but since these substances soften and melt at comparatively low temperatures they are not able to hold the bricks together if at higher temperatures these are exposed to the mechanical strains unavoidable under normal smelting conditions. Lime and its industrial mixtures, such as Portland cement, the bonding effect of which is well known, are not affected by the temperatures required to fuse the flue dust contents of the bricks, thus enabling the briquets to reach

fusion without disintegration. In presence of sulphates the lime contents of the briquets are converted into calcium sulphate, which is decomposed at a temperature of 2200° Fahr., while if silica is also present, it reacts with the sulphate, forming calcium silicate. The amounts of lime or Portland cement used in briquetting mixtures should be adopted to the composition of the flue dust mixtures and to the smelting methods adopted, and varies from 5 to 8 or 9 per cent. If carbon is present in the flue dust—which is always the case if blast furnace dust is contained in the flue dust mixtures—more lime is required. If sufficient quantities of wet flue dust are available to convert the entire mixture into a stiff mud, the percentage of lime may also be reduced to a few per cent, while if the mixtures consist of dry flue dust exclusively, the required amounts of moisture being obtained by the addition of water, 10 per cent of lime or cement may be necessary to cause sufficiently rapid hardening of the briquets.

Briquetting by Hand.—For reverberatory smelting of flue dust, the mixtures may be briquetted by hand, the only mechanical apparatus required if large quantities of flue dust are handled being a concrete mixer. The dust is roughly mixed with the appropriate percentage of lime, sufficient water added to bring the mixture to the required consistency of stiff mud, and the mass charged into the mixer. The thoroughly mixed material is now cut into small pieces by means of shovels and left to set and dry for about two days. It is then ready for smelting.

Mechanical Briquetting.—If large quantities of flue dust are to be briquetted, or if the particular grades of flue dust treated do not lend themselves to briquetting without pressure, mechanical briquetting must be resorted to. It has already been stated that flue dust containing considerable percentages of carbon such as blast furnace dust does not bind well, even in presence of more than the common percentages of lime, unless strong pressure is applied, while, occasionally, it may become necessary to even burn the bricks. If, on the other hand, flue dust is briquetted by means of sufficiently strong briquetting machines, the amount of lime or other bonding agents used may be considerably reduced. As a general rule, 3 per cent of lime will be found to be sufficient for this purpose.

Of the various briquetting machines used, the Augur machine of Chambers Bros., Philadelphia, and the presses of Chisholm, Boyd & White, Chicago, are the most commonly employed, although for general work ordinary brick-presses will give satisfactory service. For

occasional bricking of flue dust, or similar material, for instance, where a small plant desires to smelt its own flue dust twice or three

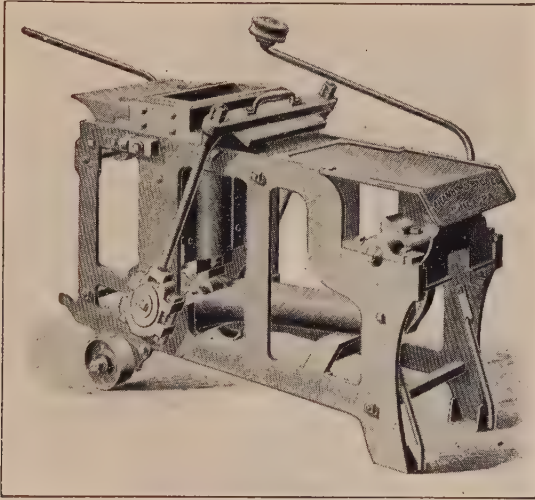


FIG. 68.—HAND OPERATED BRICKING PRESS.

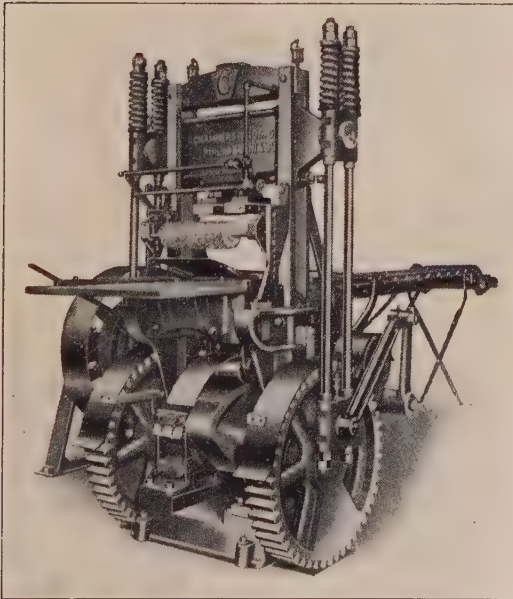


FIG. 69.—MECHANICALLY OPERATED BRICKING PRESS.

times a year, a Hand Power Brick press may prove perfectly satisfactory. Figure 68 represents a Chambers Hand Power brick press. This is a comparatively powerful press, having a steel lined box with top plate and plunger faced with steel, conveniently arranged for refitting.

Figure 69 shows a mechanically operated bricking press. This is a strongly built press of the pattern employing direct crank movement, and is so constructed that a separate and distinct pressure is applied to the lower side of the brick, in addition to the pressure from above. This is secured through the use of a hardened steel faced cam in contact with a cam roller $5\frac{1}{2}$ inches in diameter connected with the lower cross-head and causing the lower plungers to move upward through the press-box in proper time with the stroke of the double cranks giving downward motion to the upper plungers.

This press delivers a block of as much as 4 inches thickness, with a range down to $1\frac{1}{2}$ inches thickness. With endwise feed, two blocks, $12\frac{1}{4} \times 5\frac{1}{2} \times 4$ inches, may be pressed at a time, although standard brick sizes may also be made on these presses. The range of speed is from seven strokes per minute for $12\frac{1}{2}$ inch blocks to from 18 to 26 strokes per minute for standard size brick shapes.

CHAPTER XXIV

CHIMNEYS

The drawing effect of a chimney is based upon the difference between the specific gravity of the column of hot air or gases within the chimney and the same volume of cold outside air. The chimney is filled with a column of hot and, therefore, light air, while the cold outside air is correspondingly heavy, the pressure of the cold air tending to displace the lighter hot air. In passing through the firing of the furnaces this air is also heated, setting up a constant circulation.

The effective draught of a chimney is the theoretical drawing effect minus the friction losses.

The motive force is the difference between the pressure exerted by the warm air within the chimney at the base, which is dependent on the height of the chimney in feet (h), the density of the gases in pounds per cubic foot (d_1), and the pressure of the cold outside air for the same height (hd_2). Thus,

$$h(d_2 - d_1) = \text{pounds per square foot}$$

If

H height of chimney in feet

P_2 atmospheric pressure (pounds per square inch)

T_1 absolute temperature of chimney gas (degrees Fahr.)

T_2 absolute temperature of outside air (degrees Fahr.)

$$D_1 = H \left(\frac{7.64}{T_2} - \frac{7.95}{T_1} \right)$$

or for higher altitudes.

$$D_1 = 0.52 HP_2 \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

The actual effective draught obtained is less, due to friction, a working factor of 20 per cent usually being allowed for the loss of draught from this source.

The effective draught of a chimney or its draught power varies as the square root of its height, so that the draught power of a chimney 80 feet high is but twice as large as that of a chimney of a height of 20 feet. The friction of the gas current, and the loss of heat by radiation on the other hand, increase directly with the height of a chimney of equal cross-section, and it is evident that in view of these fundamental laws the height of a given chimney may reach a certain maximum, above which a further increase of draught power is practically negligible.

The cross-section of chimneys depends on the amount of gas to be passed through, which, on the other hand, corresponds to the total grate area of all the furnaces served by the chimney in question, or in the case of gas or oil burned furnaces, on the amount of fuel burned. As a general rule, the cross-section of a chimney represents 10 to 15 per cent of the total grate area, while occasionally it is increased to 25 per cent of the total grate area. This is the case where all the furnaces feeding the chimney are reverberatory furnaces used for refining or similar purposes requiring the opening of working doors for comparatively long periods. It is obvious that in determining the cross-section of a chimney, due allowance must be made for the large percentages of cold air drawn into the furnace and through the system.

Where oil or gaseous fuels are used, the cross-section of the chimneys depends upon the amount of fuel required to heat the furnaces to the required temperatures, the volume of the gases of combustion, and the proposed speed of the flue gases through the system.

Brick Chimneys.—All central chimneys of smelters, or all chimneys fed by large reverberatory and blast furnaces should be constructed of brickwork in order to prevent excessive loss of heat. The walls should be thick enough to lower the loss of heat by radiation to a practical minimum and to resist a wind pressure of 50 pounds per square inch. To further increase the stability of the chimney against wind pressure and crushing, the walls are always thicker at the bottom and the stack is tapered.

The height of the chimneys is governed by the amount of gases to be handled, their temperatures, the intended speed of flow, and the nature of the gases emitted. Chimneys should always extend above surrounding buildings, and must never be lower than 50 feet. Where the flue gases are conducted to the chimney through long flues,

and considerable resistances must be overcome, or where several flues pass into the same chimneys, its height should not be less than 100 feet. If the plant is surrounded by hills, the chimneys must either extend above their tops or be situated on top of the nearest elevation, being connected with the furnaces by sufficiently wide flues. If two or more flues unite at the base of the same chimney, the uniting streams of gas must be made to travel in the same direction, or the chimney should be divided by a vertical partition for some distance up, so that the gas currents may be all ascending before uniting. Where new connections are to be made to an old chimney, the flues should not enter the stack 5 or 6 yards above ground, as is frequently done in order to avoid trouble and expenses. The effective draught acting on the original flue at the foot of the chimney is considerably decreased by such an addition.

The lining of the chimneys used in smelters should be made of highly refractory fire-clay bricks up to at least 30 to 40 feet above the grates. The whole interior of the chimney is covered with a smooth finish of refractory mortar in order to decrease the loss of draught by friction.

A subject of considerable importance to smelters located in towns or in farming districts is the smoke nuisance caused by the presence of incompletely burned particles of fuel and obnoxious gases, such as sulphur dioxide, chlorine, or metallic vapors in the smoke. It is possible, of course, to decrease the percentage of soot and metallic vapors by controlling the combustion processes and providing for efficient flue dust and vapor collecting devices in the flue system, but it is rather difficult in the case of the average sized residue smelter to completely free the chimney gases from obnoxious contents.

Spraying devices are not in good favor with most scrap and residue treaters, the handling of the wet mud or slimes produced being more or less out of the usual line of activities. Bag filters or electric precipitating devices are too expensive to be installed in any but the largest smelters, so that the only practical way of eliminating or, at least, minimizing chimney gas troubles is to construct the chimneys as high as possible and to dilute the gases with sufficiently large quantities of air before passing them into the atmosphere.

While the admission of judicious amounts of fresh air into the flue channels is very advantageous, precipitating as it does much of the volatile metallic fumes, the drawing capacity of the chimneys is

seriously taxed, and since the chimney capacity of the majority of smelters is very limited, this dilution of the flue gases must be effected so as not to affect the draught power.

This problem may best be solved by constructing the topmost 8 or 10 feet of the chimney in checker-board fashion, as indicated in Figure 70, providing for numerous channels or air ports through which the wind may enter the chimney on all sides in an ascending direction.

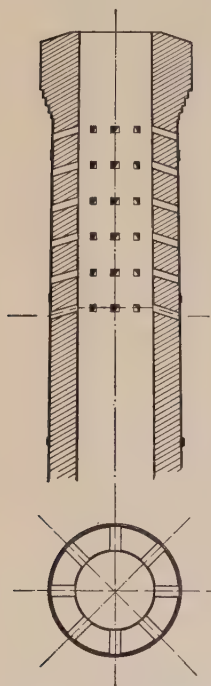


FIG. 70.—CHECKER-BOARD TYPE CHIMNEY TOP.

It is thus possible to mix the chimney gases with three or four times their own volume of fresh air within the chimney, while the thin streams of smoke leaving the chimney through the air ports are much more quickly dissolved and dispersed by the air than the heavy smoke streams emerging from the top of ordinary chimneys. The number and width of these air ports should increase towards the top of the chimney.

The drawing capacity of the chimney is not lowered by this arrangement, while under certain conditions the drawing effect may even be improved. For instance, with strong horizontal winds, the draught power of a given chimney is appreciably increased. If the air currents are directed diagonally downwards into the chimney, the chimney capacity is but little diminished, the gases, otherwise bottled up within the chimney by the pressure of the wind, being allowed to escape sideways, while the upward direction of the air currents entering the air ports actually neutralizes the downward pressure of the wind.

Steel Chimneys.—The chief advantages of steel chimneys as compared with brick chimneys are: greater lightness, strength, and cheapness, and greater speed of construction; the loss of draught power by friction is appreciably smaller. The disadvantages, which disqualify steel chimneys for many purposes, are: a vastly greater loss of heat by radiation, and comparatively poor durability.

On account of their high degree of thermal conductivity steel chimneys are usually lined with refractory bricks, thus sacrificing the advantage of lower frictional resistance of steel chimneys.

These deductions do not apply to the small steel or sheet iron chimneys usually employed to provide the draught for small single units such as melting pots, small oil or gas fired reverberatory furnaces, etc., which are usually erected on top of the furnaces and brought out through the roof of the building. As a rule, the gases entering these chimneys are hot enough to permit of a considerable loss of heat by radiation without causing a corresponding loss of draught power, while in many cases the flue gases remain hot enough to endanger any woodwork approaching too near the chimney walls. It is absolutely necessary, therefore, to cut away all combustible building material within about 15 inches of the chimney, closing the holes with suitably shaped sheet iron or asbestos sheet sections.

Concrete Chimneys.—It appears that the superior qualities of reinforced concrete chimneys are not sufficiently realized by metallurgists. Combining the high tensile strength and the lightness of bricklined steel stacks with the strength and longevity of brick chimneys, their erection is very rapid, and the costs of erection and maintenance is noticeably lower than those of brick chimneys. In common with all concrete constructions, the erection of reinforced concrete chimneys must be closely supervised, but a well-built chimney of this type will outlast any other type of chimney used for the same purpose. Since concrete materials are rather sensitive towards elevated temperatures and temperature fluctuations, it is necessary to provide them with a refractory lining up to about 50 or 60 feet above the base.

CHAPTER XXV

SAMPLING OF SCRAP AND RESIDUES

Not very many years ago, sampling was considered more or less of a simple mechanical operation to be entrusted to some old laborer attached to the chemical laboratory, while in many instances, this field of application was considered an ideal hunting ground for sharp-witted individuals, who by means of increasingly cunning tricks and by the application of simple mechanical and physical principles were able to influence the results of tests, or the metal contents of the sample, one way or another, according to the interests of their principals.

One of the common tricks calculated to force up the metallic contents of dry residue samples, and applicable any windy day was—or is—to shovel the residues from some high platform, such as a railroad car down to the ground, giving the shovel as liberal a sweep as possible and thus permitting the wind to carry off comparatively large percentages of light, earthy material. By this method it is easily possible to increase the metal contents of a sample by from 3 to 5 per cent.

Another profitable method of inducing a certain degree of separation is to cultivate the habit of stumbling. An interested sampler, carrying a container of dry residues rich in metallic particles may, by a skilful series of stumbles, cause a noticeable segregation of the metal at the bottom of the container. Careful emptying of the receptacle previous to quartering will cause the enriched portion of the sample to be located at one side of the heap. There are numerous other tricks of the trade calculated to correct the fortune of sampling and this fact as well as the rapidly increasing recognition of the importance of this phase of work caused sampling operations to be lifted out of the sphere of chance and skill, and to be put upon a strictly scientific basis founded upon the fundamental laws of averages and probabilities. This fact is best demonstrated by the class of men now recognized as expert samplers, who, apart from

a thorough knowledge of the many metallurgical products and of the principles of sampling in general, are usually conversant with the various principles of mining, metallurgy, assaying, casting and marketing fundamentally related to their profession. Many samplers are expert analysts, and the importance generally placed on the work of these men is indicated by the fact that in large smelters the head sampler is usually paid a higher salary than the Chief Chemist.

The Law of Averages and Probabilities.—It would lead too far here to discuss the law of averages and probabilities at greater detail, and the attention of the interested reader is called to the various special publications on this subject, one of the most instructive of which is “The Principles and Practice of Sampling Metallic Metallurgical Materials” by E. Keller. The important principle of these laws, expressed in a few words, is that the unavoidable chance errors of the average sample can be reduced to very narrow limits if a reasonably large number of samples are averaged by accumulation and this raw average be sampled down for analysis.

For instance, if in sampling 500 white metal ingots of theoretically uniform composition every fifth ingot is sampled by drilling, and if the mean departure from the true average composition in each sample is 5 per cent, one way or the other, the laws of averages and probabilities holds, that if the hundred samples taken are accumulated and cut down to an analytical sample, the probable error of the complete sample will be about 0.20 to 0.25 per cent.

Considering the physical state of the various raw materials, and the intermediate and finished product and residues handled by residue and scrap treating works, these may be subdivided into the following groups:

1. Ashes and similarly finely divided materials of uniform composition.

- a. dry, and b. wet.

2. Ashes and similar material made up of fines, coarse material, and lumps.

3. Ashes and similar materials containing various proportions of metallic constituents derived from the same source. (Dross, globules, skimmings, etc.)

4. Ashes and similar materials, with or without non-ferrous metallic constituents, containing various proportions of iron scrap. (Remelted zinc ashes, etc.)

5. Non-ferrous scrap consisting of uniformly small pieces of the same origin.
6. Non-ferrous scrap composed of large pieces of similar origin.
7. Mixed scrap, large and small, composed of variously alloyed material. (Red metal scrap, white metal scrap, aluminum alloys, zinc scrap, etc.)
8. Red metal scrap containing various proportions of white metal, plated or cast on.
9. White metal scrap containing various proportions of red metal alloys, plated on, screwed or hammered into the white metal castings.
10. Borings, filings, and similar metallic scrap, free from contamination with dirt or foreign materials.
11. Mixed borings, filings, etc.
 - a. clean,
 - b. dirty (shop sweepings, etc.)
 - c. wet.
12. Ingots of various compositions.
13. Metallic foil, etc., mixed with, or free of waxed paper, paper board, tin boxes, etc.
14. Slags, matte, speise.
15. Dross, skimmings, etc.

Sampling of Metal Ingots.—For the purpose of sampling, ingots are generally divided into two groups, ingots of metallic alloys liable to liquation or segregation during pouring, such as zinc alloys, bearing metals, bronzes or other copper alloys rich in lead, etc., of which 3 to 5 per cent are usually set aside as preliminary sample, and ingots of simple metals, copper, tin, zinc, lead, antimony, aluminum, etc., or of alloys forming perfect solutions, where 2 per cent of the total amount of metal will suffice to give a fair average sample.

The above applies to large lots only, of course, and the percentual number of ingots taken as samples increases with decreasing size of the lot. For instance, if the total number of ingots making up a lot is about 100, a 10 per cent sample would appear appropriate, while with smaller lots, percentages varying from 15 to 25 per cent should be taken, the exact figure in each case depending on the nature of the alloys.

From sample ingots and large pieces of scrap, samples are drawn by means of sawing, boring, or filing, sawing being generally con-

sidered to represent the most dependable method of sampling. Both sawing and drilling operations must be carried out without the use of oil or soapwater, since subsequent washing of the chips or drillings with water or other solvents induces the danger of surface oxidation, even if the samples are thoroughly dried immediately afterwards.

Boring should be effected with a mechanical drilling machine operating a $\frac{3}{8}$ to $\frac{5}{8}$ inch drill. If possible, the ingot should be bored clean through; if not, one hole should be drilled from both sides of the ingot down to its center. Since all metallic surfaces are usually covered with a film of oxide or dirt, the first chips should be disregarded. If in drilling ingots composed of heterogenous material small chips are also produced, the drillings should be reduced to the size of these chips. Where this is impossible, the drillings should be screened and the proportion of fine and coarse material determined, or the drillings may be melted in a crucible, and a fair average sample be taken by "dipping."

The melt, representing the fused sample, may be sampled by dipping, and shotting, or by sawing, filing, or boring the ingots or slabs poured from the melt.

In melting down a sample and subsequent sampling, attention should always be paid to the various physical and metallurgical properties of the materials in question. In the case of simple metals, containing varying percentages of impurities, the melting points of the metals alone need be considered, while the treatment of alloys requires consideration of heterogeneity, due to different melting or freezing points of the various constituent phases of the alloys or to widely differing specific weights. This latter factor may become very noticeable even with impure simple metals, as, for instance, with remelted zinc, where it is difficult, indeed, to mix zinc and the few per cent of lead present sufficiently to draw a fair sample, even if the bath is stirred during sampling. If the metal temperatures are high enough heterogeneity will not make itself felt so much in the pot or crucible, but very queer results are sometimes obtained on pouring the sample. It appears self-evident that all samples are poured in chill molds, but even these will not always prevent segregation and diffusion, although if the molds are sufficiently shallow and entirely cold, noticeable differentiation of the composition of the alloys in different parts of the flat ingots may be considered an exception.

The sampling method most susceptible to the danger of segregation and diffusion is the pouring of the entire sample melt into molds,

and drawing a final sample by drilling, sawing, or filling the ingots. Segregation in this case may take place in the melting pot, or crucible, as well as within the mold. Pouring a dip sample into a cold flat mold is practically faultless if the melt is thoroughly stirred a few minutes before as well as during pouring. However, in radical cases, as for instance, with mixtures of metals which do not alloy in the proportion present, such as aluminum-lead mixtures, and which on account of greatly differing specific weights tend to separate quickly, best results may be obtained by "shotting" into water. A dip sample is taken out of the vigorously stirred bath, and the ladle emptied in a wide sweep into a sufficiently large bath of water, to produce small metal pellets easily sampled. It goes without saying that previous to sampling these shots must be dried for at least 30 minutes at a temperature of 230° Fahr.

Sawing the sample ingots should be effected under a mechanical sawing machine, the ingot being clamped down in such a way as to permit the saw to cut through one side of the ingot down to its center. Sawing from the bottom or the top side of the ingot would not take into consideration possible eliquation or segregation phenomena.

The ears of white or red metal ingots, especially white metal alloys containing considerable percentages of antimony, should never be used as sample, since on account of liquation of the constituents, the composition of the ears may not represent that of the ingot proper. Experiments cited by L. Parry¹ gave the following results:

(a) A pot of lead-antimony alloy made from 75 parts market lead and 25 parts refined antimony was sampled from the pot and the sample assayed for antimony. It showed 24.9% Sb. The metal was then ladled out into square-sectioned ingot molds with end ears. When cold, an ear was broken off one of the pigs and assayed for antimony by the same method as before. It showed 28.6% Sb.

(b) A pot of metal was made up from lead and antimony to hold 17 per cent antimony. It was sampled from the pot, and the sample showed 17% Sb by assay. Samples were then taken from different parts of the same pig and assayed as follows (the pigs were about 6 in. deep and weighed about 80 lb. each):

1. End of pig (ear): 19.7% Sb.
2. Top of pig (center, 2 in. from surface) ÷ 22.6% Sb.
3. Bottom of pig (center, 1 in. from bottom): 11.4% Sb.

¹ Notes on Alloys, p. 49.

The entire pig was melted and a small sample taken with a ladle; this showed 17% Sb by assay. The sample taken from near the bottom of the pig approximates in composition to the eutectic alloy of lead and antimony.

(c) A sample of several tons of pigs of American antimonial lead, taking chips from opposite top and bottom edges of each pig, melting chips in ladle, and pouring in sample ingot mold, showed by assay: 29.1% Sb, 0.80% Cu, 0.55% As, 0.85% Sn.

(d) Sample of same pigs taken by melting the pigs in a pot, and after mixing taking small samples from the pot, showed by assay: 28.6% Sb, 0.90% Cu, 0.65% As, 0.80% Sn.

The results of these tests prove that wherever possible, that is to say, wherever the amount of the sample is not too large, the sample should be taken from the pot or crucible of molten metal, which must be thoroughly fluid and well stirred before and while taking the sample.

Before reducing the total quantity of borings, filings, or chips to regular sample size, the material must be freed from metallic iron by means of a strong magnet, the percentage of iron being determined.

Reduction of the total sample is usually effected by the quartering methods. After shoveling over the sample sufficiently often to assure of the uniform composition of all parts of the sample, this is "coned" by piling up the material on a thoroughly cleaned section of the floor or a table, taking care that every shovelful of material is thrown directly on the top of the cone, so that it may descend and spread evenly down the sides. The cone is then truncated until it forms a flat circular heap, which is quartered by drawing two diametrical lines across the surface of the heap at right angles to each other. Two opposite sections are removed and discarded, while the two other sections are again mixed and piled up into a smaller cone, which is truncated and quartered as before. This process is repeated until the sample is reduced to the amount necessary for the various test samples.

New Metals and Alloys.—Since practically all new metals and alloys are sold or bought in form of ingots or slabs, reduction of the first sample, representing from 2 to 5 per cent of the lots, depending upon the value of the materials and the typical degree of homogeneity of the alloys sampled, is always carried out by sawing or drilling. Borings should in all cases be reduced to uniform small pieces by

hammering or stamping. The percentual amount of sample to be taken in each case is as follows:

Virgin Aluminum	2%
Remelted Aluminum	5%
Aluminum Alloys	5%
Spelter and Refined Zinc.....	2%
Remelted and Quality Zinc.....	3%
Work Lead and Refined Lead.....	2%
Secondary Refined Lead.....	3%
Zinc Alloys	5%
Original Pure Tin.....	2%
Secondary qualities (less than 96% pure).....	5%
Virgin Antimony	2%
Lead Alloys containing tin and small amounts of antimony.....	3%
Lead Alloys containing up to 10% tin and considerable amounts of antimony	5%
Lead Alloys, bearing metals, etc., containing more than 10% of tin	2-4%
Britannia Metal, etc.	3%
Tin Alloys, containing more than 40% tin and small percentages of antimony	2%
Electrolytic and Refined Copper.....	2%
Anodes or impure Copper.....	5%
Bronzes	2%
Brasses	2%
Red Brasses, German Silver, etc.	2%

Sampling of Old Metal Scrap.—Aluminum scrap may consist of old or new sheet aluminum, mixed aluminum scrap, or old cast aluminum scrap.

If the lot consists of old or new sheet aluminum only, 2 per cent are taken for a sample, which is cut from as many sheets as possible. The sample is weighed and then cleaned and freed from all foreign substances, the cleaned and dried sample to be weighed again. This first sample is reduced to about 1 to 2 pounds by cutting small pieces off each of the pieces of sheets making up the first sample. This final sample is mixed thoroughly and divided up into test samples.

Mixed aluminum scrap or old cast aluminum scrap, due to their strongly differing compositions, require the extraction of much larger

samples. The percentual amount of sample necessary depends upon the fair judgment of the sampler, but should not amount to less than 4 or 5 per cent, which is melted down in a large crucible furnace. If the sampler is not thoroughly expert at melting down aluminum scrap, the sample should be placed into a locked and sealed container and further treatment entrusted to an expert.

The sample is melted down at a temperature of about 800° C. (1472° Fahr.), the larger pieces being melted down *qrst.* The ashes and dross are carefully removed, crushed until on screening only metallics remain on the screen, and the fines weighed and sampled by quartering. The metallics are freed from iron by means of a magnet, the weight of the iron noted, and the metallics reduced to about 1 or 2 pounds by quartering. The metallic aluminum remaining in the crucible is poured into thin slabs and a sample is taken by sawing or boring.

Aluminum alloy scrap is treated like mixed aluminum and cast aluminum scrap, the minimum size of the final sample being 5 per cent.

Old Zinc and Zinc Alloy Scrap.—If the lot consists of fairly uniform material, such as old sheet zinc scrap, or zinc-aluminum scrap derived from similar sources, 10 per cent are taken for a sample, while with mixed scrap the sample should amount to as high as 25 per cent, depending upon the appearance of the material and the fair judgment of the sampler. The whole sample is melted down in an iron melting pot, and the metal cast into thin slabs, which are then sampled as usual, by sawing or drilling. The ashes are crushed until on screening only metallic materials remain behind on the screen. The fine ashes are weighed and sampled by quartering. The metallics are freed from iron by means of a magnet, the weight of the iron determined, and the metallics sampled by quartering, if sufficient of this material has been obtained.

Old lead scrap, consisting of lead tubes, rests of tubes, sheet lead, soft lead pellets, and bullets, etc., if free of other materials, requires a sample of 5 per cent, which is melted down in iron melting pots, the metal, ashes, and iron being weighed and sampled as usual.

Old Tin Scrap, Stanniol, and Condenser Foil.—Of this material, excepting condenser foil, 10 per cent are taken for a sample, which is melted in a cast-iron melting pot. The various products are weighed and sampled as usual.

Condenser foil material is one of the most difficult scraps in the

market. The first sample should amount to from 3 to 5 per cent of the lot. In many instances, the rolls are unwound and burned in an iron crucible, most of the tin being converted into ashes; metal and ashes are then weighed and sampled as usual. Where it is agreed upon by the interested parties to work with smaller samples, the first sample may be reduced to 2 or 3 pounds. The rolls of foil are carefully unwound and the metallic foil separated from the waxed paper. The metallic material is then pressed together and melted down in a small iron pot, metal and ashes being weighed and sampled as usual.

Old Bearing Metal and Solder Scrap, etc.—Ten per cent of the lot is taken for a sample, which is treated like lead and tin scrap.

Electrolyte Shells: or Plates.—Although according to specifications this material must be hand-picked and free from dross, a considerable amount of white metal is always left behind, rendering this material unfit for use in high grade alloy production. If electrolyte shells are present in regular copper scrap, it must be picked out carefully, of course. If present in lot size, 5 to 10 per cent of the material is drawn as sample, which is melted down in graphite crucibles, the metal, ashes, slags and insoluble or infusible material being determined and sampled as usual.

Sampling of Borings, Filings and Similar Scrap Materials.—On account of the widely differing properties of the numerous metals and alloys, and in view of the pronounced influence of the individual mechanical and chemical properties on the treatment of the thin-walled and finely divided materials, sampling methods must be adapted to the characteristics of the samples in each and every individual case. It is necessary, therefore, to consider the most important metals and groups of alloys separately.

Aluminum Borings and Chips.—Ten per cent of the shipment are drawn as first sample, which by careful mixing and quartering is reduced to a final sample of from 5 to 10 pounds. Lumpy material must be pulled or cut apart until the entire first sample consists of a thoroughly mixable mass. Moisture, iron, and oil contents are determined, and the dried sample is divided in fine and coarse portions by screening. Non-metallic contents of the material are separated from the first sample and their weight determined. The alternative method of treating non-metallic constituents, that is, crushing and uniting with the fine portion of the sample, does not appear to give dependably fair results.

The sampling of *zinc borings and chips* does not differ materially from the method applied to aluminum materials. As a rule, smaller first samples are taken, while instead of determining the proportion of fine and coarse material in the original sample, the zinc borings and chips are broken up by stamping or crushing, and the resulting mixture is divided into fine and coarse portions by screening.

White Metal Alloy Borings and Chips.—If the lot of borings, etc., consists of uniform material, 10 per cent are taken for a sample. This sample is melted together in an iron melting pot. Iron and other infusible material as well as the ashes are removed separately and their weights determined. The melt is then stirred for a few minutes and a sample ladled out while stirring. This sample is immediately poured out over a cold iron plate so as to insure practically instantaneous solidification and to prevent liquation. The final sample is then prepared by drilling or sawing the cold metal plate. The first sample must always be melted down in one pot.

Mixed white metal alloy borings and chips should not be sampled by reducing the lot to a 10 per cent sample. A fair average sample is only obtainable if the entire lot is melted down and a sample is obtained by dipping. If the available melting pots are not large enough to take up the entire lot, this may be melted in several melting pots, the proportional weight of infusible material and ashes being determined as above.

Mixed Red Brass and White Metal Chips.—A 10 per cent sample of this material may be treated by one of the following three methods in accordance with the character of the material and the agreement reached between the interested parties.

(a) If it is desired to roughly determine the proportion of white and red material by sampling, the first sample is reduced by mixing and quartering to a final 3 pound sample, and the fines removed by screening. The coarse white and red metal chips are then separated by hand-picking. The proportion of the fine to coarse material and that of the coarse white to the coarse red chips are then determined by weighing.

(b) The sampling method most generally applied consists of reducing the sample to from 5 to 10 pounds, crushing the material to approximately uniform size, removing the iron by means of a strong magnet, and dividing the carefully mixed final sample into the various sample portions.

(c) A third, but doubtlessly faulty sampling method is to reduce

a large first sample to about 150 pounds, remove the iron by means of a magnet (determine the weight), and to melt the sample in a graphite crucible, pouring the metal into thin plates. The final sample is taken by sawing or drilling. The slag produced is crushed until, when screened, only metallic material remains on the screen. Both metal and powdered slag are carefully weighed and sampled.

Sampling of Metallurgical and Chemical Residues.—Metallurgical and chemical residues include all ashes, slags, dry drosses, pastes, slimes, and similar material containing most of their metallic contents in a chemically combined state.

All dry residues of this type should be sampled by quartering down a first sample comprising in practically all instances 10 per cent of the shipments. The methods employed in taking the 10 per cent sample depend upon the condition of the sample and the judgment of the sampler. If the material is shipped or handled in barrels, bags, boxes, etc., an appropriate quantity is taken from each container, the proportion of fine and coarse material (lumps) being left to the discretion of the sampler. If the material to be sampled is being loaded into, or unloaded from, railroad cars, 1 of every 10 shovels is retained as sample.

If the residues are too wet to be sampled by the quartering method, the first sample may be deposited in a large flat container, and reduced by taking a few shovelfuls of material out of the thoroughly stirred mass. As a rule, from 5 to 10 shovelfuls make a second sample, while after mixing this quantity, one shovelful of material is taken out, representing the final sample.

Residues of distinctly slimy consistency may be sampled by the tube method, a sufficient number of tubes full of the material being drawn from the lot to make up a 10 per cent sample, which is carefully mixed and a smaller amount taken as second sample. If slimy residues are sampled from barrels or boxes, the tube sampling method may also be resorted to, although in this case it appears perfectly safe to extract one or a few shovelfuls from the different containers.

Aluminum Residues.—Ten per cent are taken as sample. If the sample contains lumps, these must be broken up and mixed with the rest of the sample. This first sample is then reduced to about 10 pounds by quartering and the moisture determined. The sample is then further disintegrated and, finally, screened until only metallic particles remain on the screen. If the metallic ingredients of the sample consist of pieces of greatly varying size, they should also be

divided into a finer and a coarser grade. The iron contained in the sample is separated by means of a magnet and the exact percentage determined.

Zinc Residues.—Straight zinc ashes such as are produced in zinc melting or zinc plating works also require a 10 per cent sample, which is reduced by quartering to about 10 or 15 pounds. This sample is dried at 230° Fahr. and by repeated stamping and screening separated into a fine, medium, and coarse grade, which should be placed and kept in air-tight receptacles.

Zinc slags, containing ammonium chloride, are quickly quartered down to about 10 pounds. The sample is then broken up until everything passes a 1/3 inch screen. Larger pieces of metallic material are hammered down to pass this mesh, and the various test samples are then immediately deposited in air-tight containers. The entire sampling operation must be carried out as rapidly as possible in order to preclude the absorption of excessive amounts of moisture by the strongly hygroscopic material.

Tin Residues.—These residues may consist of *tin scruff*, containing besides large pieces of metal, considerable percentages of free hydrochloric acid and zinc chloride, *tin plates*, derived from chemical works, and containing from 45 to 55 per cent tin and 5 per cent chlorine, various types of *tin precipitate*, *tin chalk*, *tin grease*, etc. Also straight *tin ashes*, *tin drosses*, and various other metallurgical residual products.

All the various chemical tin residues are too wet, as a rule, to be sampled by quartering. Ten per cent samples are usually taken, therefore, by reserving every tenth shovel of the material for the first sample. The accumulated first sample is then stirred and a few 1/4 shovel samples taken from different parts of the lot. This final sample is either mixed and immediately placed in air-tight receptacles, or it is dried at 230° Fahr., the moisture determined, and the dry material ground fine. If on screening, metallics remain back on the screen, this is melted together in a small melting pot. The metal is sampled by taking a dip sample from the well-mixed bath. The ashes are added to the original sample, everything mixed, and reduced to about 1 pound by quartering.

Tin Slags.—The ten per cent sample is powdered in ballmills, etc. The metallic particles obtained by screening are weighed and melted. The metal is sampled as usual, and the ashes weighed and sampled separately. The powdered slag is reduced to about 2 pounds by

quartering. If ballmills or larger powdering machinery are not available, the first sample is broken up so as to permit of the taking of a fair average sample. It is then reduced to about 10 or 15 pounds by quartering and this sample treated as above indicated.

Dry Tin Ashes.—The original 10 per cent sample is reduced to 20 pounds by quartering, this second sample ground and the metallies separated by screening. The metal is weighed, melted and sampled as usual. The ashes are added to the original sample, which is thoroughly mixed and reduced to about 2 pounds by quartering. Moisture and iron is determined from about 2 or 3 pounds taken separately from the second sample. The moisture is determined first and the iron separated by means of a magnet.

Dry Tin Drosses.—The 10 per cent sample is crushed to practically uniform size and screened to separate as much of the ashes from the metallic material as possible, both of which are weighed. The metal is melted down in a melting pot, the ashes taken off and added to the first ashes. The metal is sampled as usual, while the carefully mixed ashes are reduced to a 2 pound sample by quartering.

Lead Residues.—*Lead Gruff*, containing besides 23 to 28% lead, about 30% iron, and about 30% soluble lead salts, and representing a by-product of cyanide manufacture, *Battery Waste* and *Old Accumulators*, containing from 65 to 95% lead in form of Pb, PbO, and PbO₂, various lead salts, *White Lead Waste*, *Paint Skins*, and metallurgical residues such as *Lead Ashes*, *Slags*, and *Slimes*.

The sampling of lead residues does not differ in any way from that of tin residues of similar nature and consistency. If the residues contain chlorine or sulphur, moisture determination should not be made, the final sample being drawn as quickly as possible and placed in air-tight receptacles.

Lead slimes may also be sampled like tin residues of similar consistency, although occasionally the following method is used: After weighing the individual barrels, they are opened, half of the contents removed, and one or two shovels of the material extracted as a sample. The sample in a metal container, weighed before and after filling, is carefully mixed, and a final sample of about 5 to 10 pounds drawn, which is dried at a temperature of not less than 500° Fahr. The loss of weight by evaporation is determined, and the dry residues ground into a fine powder, which is reduced to about 1 pound by quartering.

Particular attention must be paid to the sampling of battery scrap, consisting of plates in various states of decomposition, while the lesser qualities contain considerable percentages of battery plate mud. Since the shipments are made up of plates, lugs, separators, and mud, the difficulty facing the sampler is to get fair ratios of these components, of which the lugs contain by far the largest percentages of lead. It is necessary, therefore, after drawing a first sample, representing from 5 to 10 per cent of the lot, to remove the lugs and to determine the percentage.

White Metal Alloy Residues.—*Terne Ashes* from tin plate works, *Solder Ashes*, *Babbitt Ashes*, *Composition*, *Pewter*, and *Type Ashes*, etc., are all sampled like tin and lead residues.

The Moisture Determination.—As a rule, the general sample will suffice for this purpose, although in many instances, as, for instance, where high water contents render the drawing of a uniform sample impossible and the entire lot must be subjected to preliminary drying, a special sample should be prepared for this purpose.

Speaking generally, all materials excepting ingots and heavy scrap require the determination of moisture, while occasionally oil and grease, or other organic materials are also removed and determined by heating the samples.

In taking, preparing, and preserving the moisture sample, the following factors should be considered:

1. Where samples must be taken from large piles of residues or from freight cars after prolonged periods of transportation, the surface layers will always show less moisture contents than the lower strata, although if the material has been subjected to rain, the reverse condition may prevail. Materials sampled in the holds of ships, on the other hand, may prove to be soaking wet at the bottom and comparatively dry on top.

2. Moist materials may lose a considerable percentage of moisture unless sampled down as quickly as possible and placed in air-tight receptacles immediately.

3. Dry materials, containing hygroscopic ingredients, such as zinc chloride, etc., may absorb moisture during sampling. Rapid sampling and immediate air-tight packing is also required in this case, therefore. While bottling or packing the final samples in tins or other air-tight containers may be considered a general practice among reliable samplers, less care is usually observed in regards to the speed of sampling.

Under extreme conditions it may prove to be necessary to eliminate as large a part of the open air sampling as possible by providing for a large and fairly moisture-proof box, or a large barrel provided with a well-fitting cover. The various parts of the sample are then placed into this container directly on taking, and the cover opened only for the introduction of fresh sample material. Upon filling the container, this is emptied, coarse pieces are broken up, and the sample is quickly quartered down to about 3 to 5 pounds, which is weighed and dried in a drying closet at a temperature of not more than 215° Fahr. Lower temperatures may cause the retention of some of the moisture, while higher temperatures may cause not only the evaporation of oil and other organic materials, which, if present, should be determined separately, but a noticeable degree of oxidation as well. T. A. Wright, of Lucius Pitkin, Inc., in a recent lecture held before the Am. Inst. of Min. & Met. Engineers pointed out that materials like copper cement and some mattes will show first a loss, but finally a gain when dried at slightly over 212° Fahr. The drying period should not be pre-determined but must be prolonged until the weight of the sample remains constant, the weight being determined after cooling the sample to room temperatures.

Determination of Loss of Weight by Burning.—Certain samples such as turnings, sweepings, etc., usually contain appreciable quantities of oils and fats, while numerous residues such as flue dust or liquation residues may contain carbon or other organic materials, all of which are usually eliminated and determined by heating the sample to redness. While this method may give good results in sampling copper or copper alloy scraps and residues, it is obvious that the results obtained by heating white metal materials to redness are bound to be decisively influenced by volatilization of metallic constituents in one direction and by oxidation in the other. Where the determination of organic substances by the burning method is objected to by one party, the oil and fat contents of metallic scraps must therefore be determined by washing first with alcohol and then with ether. If the sample contains moisture, it must first be dried, since water is eliminated by either method.

Determination of Metallic Iron Contents.—If possible, metallic iron is to be removed and determined with a strong magnet, and where the iron is firmly attached to the castings or manufactured material scrap, or if it is contained in, or surrounded by, white metal, it is picked out by hand, or skimmed off, directly after melting down the sample. If it is possible to separate the iron by sweating

off the white metals, this method is to be preferred. In contrast to red metal alloy scrap, the removal of iron from white metals does not involve the danger of absorption or solution of the iron by the melt. A certain small loss of iron by solution may be incurred in the case of zinc sheet scrap, but since with careful operation this loss need not exceed 0.05 per cent or less, it is considered negligible. The small film of metal usually adhering to the iron removed by melting down or liquating the white metal may usually be knocked off while the iron is still hot, while the amount of the very small rests of metal still remaining must be judged.

STANDARD SCRAP METAL DEFINITIONS

Tentative Recommendations for Stabilizing the Buying and Selling of Secondary Metals

Recommended by the Metal Division of the National Association of Waste Material Dealers

General Application

A. Free Metal.—By free metal is meant that metal is present alone, or in combination with one or more other metals as an alloy, and not that metal present as an oxide, silicate, slag or similar compound.

Example: Drosses, spatters, skimmings, battery lead, zinc dust.

B. Available Metal.—The term available metal shall be confined to the valuation of zinc dust and aluminum skimmings, drosses and ashes, and shall denote the recoverable metal figure or value, obtained by means of a specified method agreed upon beforehand, unless at some future date a standard method shall be presented and accepted.

C. Metallics.—This is a technical term used by chemists in sampling and analysis to define the amount of metal left on a screen or screens, when pulverizing and preparing samples. The terms "seals" and "coarse" are often used instead. In preparing samples there may be more than one size or mesh of "metallics."

Example: For all metals.

D. Total Metallics.—This term covers all metallics other than that contained in the "fines" and is, therefore, also a technical term of the chemist.

Example: For all metals.

E. Fines.—By fines is meant the portion of the material passing through some certain mesh of a screen. It is sometimes called “pulp” to distinguish it from “fines,” consisting of all, or containing considerable, free metal.

Example: For all metals.

Fire Assay

F. Metallic Button.—The term metallic button shall be used only in connection with the fire assay of (a) copper turnings and borings, in which case it is taken to mean the after-melting weight of a sample of turnings, borings or grindings from composition, red or yellow brass or copper metal; (b) battery lead and leaded drosses, in which case it is taken to mean the weight of the melted metal obtained by fluxing a sample with soda and charcoal; (c) tin dross, in which case, it is taken to mean the weight of the melted metal obtained by melting a sample under cyanide.

Notes: When the term “metallic button” is used in a contract, it is understood that the amount of metal remaining in the slag, dross or oxide is disregarded.

It is to be further noted that while the use of the fire assay method is recognized by the committee, this recognition is in no way an endorsement of it as good trade practice, but that on the contrary, they feel it is to the best interests of the industry to encourage the valuation of secondary metals by chemical analysis, as in the mining industry.

Wet Assay or Chemical Analysis

G. Metallic Contents.—This term is taken to mean the assay value of the metals paid for and/or penalized as determined by chemical analysis.

Examples: Lead and/or antimony in battery lead; copper and/or tin in composition; lead, tin, antimony, copper in babbitt, etc.

H. Metallic Yield.—This shall be ascertained by subtracting a definite percentage of the metal or metals from the assay value (or metallic contents). To illustrate:

Total lead antimony (metallic contents) less 1.5 per cent metallic yield.

Copper assay (electrolytic or its equivalent) less 1.3 per cent metallic yield.

I. Metallic Recovery.—It is further recommended that the terms “metallic recovery” be refused recognition by this association for the subjoined reasons:

“Metallic recovery” is essentially a term used by metallurgists, chemists, etc., and its meaning is so general that its use should be confined to plants, works, processes, etc.

The committee also recommended that, until such time as standard methods of sampling and analysis are drawn up, on materials handled by the members of this Association, the methods of analysis to be used shall be those jointly agreed upon by the chemists of the buyer and seller unless (1) the method is named or outlined in the contract, or (2) covered by the specifications of the American Society for Testing Materials.

CHAPTER XXVI

STANDARD CLASSIFICATION FOR OLD METALS ¹

Adopted by the National Association of Waste Material Dealers, Inc.
(Circular K)

1. Delivery.—(a) Delivery of more or less on the specified quantity up to $2\frac{1}{2}$ per cent is permissible.

(b) If the term “about” is used, it is understood that 5 per cent more or less of the quantity may be delivered.

(c) Should the seller fail to make deliveries as specified in the contract the purchaser has the option of cancelling all of the uncompleted deliveries or holding the seller for whatever damages the purchaser may sustain through failure to deliver and if unable to agree on the amount of damages, an Arbitration Committee of the National Association of Waste Material Dealers, Inc., appointed for this purpose, to determine the amount of such damages.

(d) In the event that buyer should claim the goods delivered on a contract are not up to the proper standard, and the seller claims that they are a proper delivery, the dispute shall be referred to an Arbitration Committee of the National Association of Waste Material Dealers, Inc., to be appointed for that purpose.

(e) A carload, unless otherwise designated, shall consist of the weight governing the minimum carload weight at the lowest carload rate of freight in the territory in which the seller is located. If destination of material requires a greater carload minimum weight, buyer must so specify.

(f) A ton shall be understood to be 2000 pounds unless otherwise specified. On material purchased for direct foreign shipment a ton shall be understood to be a gross ton of 2240 pounds unless otherwise specified.

(g) If, through embargo, a delivery cannot be made at the time specified, the contract shall remain valid, and shall be completed

¹ Effective from March 1, 1928.

immediately on the lifting of the embargo, and terms of said contract shall not be changed.

(g) 1. When shipments for export for which space has been engaged have been delivered or tendered to a steamship for forwarding and through inadequacy of cargo space the steamship cannot accept the shipment, or where steamer is delayed in sailing beyond its scheduled time, shipment on the next steamer from the port of shipment shall be deemed a compliance with the contract as to the time of shipment.

(h) In case of a difference in weight and the seller is not willing to accept buyer's weights, a sworn public weigher shall be employed and the party most in error must pay the costs of handling and reweighing.

(i) When material is such that it cannot be sorted by hand, consignees cannot reject the entire shipment if the percentage of rejection does not exceed 10 per cent. The disposition of the rejected material should then be arranged by negotiations; no replacement of the rejected material to be made.

Upon request of the shipper, rejections shall be returnable to the seller on domestic shipments within one week and on foreign shipments within thirty days from the time notice of rejection is received by them and upon payment by them of 1c a pound on material rejected to cover cost of sorting and packing; the seller to be responsible for freight both ways.

2. No. 1 Copper Wire.—To consist of cleaned untinned copper wire not smaller than No. 16 B. & S. Wire gauge to be free from burnt copper wire which is brittle and all foreign substances.

3. No. 2 Copper Wire.—To consist of miscellaneous clean copper wire which may contain a percentage of tinned wire and soldered ends but to be free of hair wire and burnt wire which is brittle; the tinned wire not to be over 15 per cent of the total weight.

4. No. 1 Heavy Copper.—This shall consist of copper not less than 1/16 inch thick, and may include Trolley wire, Heavy Field wire, Heavy Armature wire, that is not tangled, and also new untinned and clean copper clippings and punchings, and copper segments that are clean.

5. Mixed Heavy Copper.—May consist of tinned and untinned copper, consisting of copper clippings, clean copper pipe and tubing, copper wire free of hair wire and burnt and brittle wire, free from nickel plated material.

6. **Light Copper.**—May consist of the bottoms of kettles and boilers, bath tub linings, hair wire, burnt copper wire which is brittle, roofing copper and similar copper, free from radiators, brass, lead and copper connections, readily removable iron, old electrotype shells and free of excessive paint, tar and scale.

7. **Composition or Red Brass.**—May consist of red scrap brass, valves, machinery bearings and other parts of machinery, including miscellaneous castings made of copper, tin, zinc and/or lead, no piece to measure more than 12 inches over any one part or to weigh over 60 lbs., to be free of railroad boxes, and other similarly excessively leaded material, cocks and faucets, gates, pot pieces, ingots and burned brass, aluminum composition, manganese and iron.

8. **Railroad Bearing.**—Shall consist of railroad boxes or car journal bearings, must be old standard used scrap, free of yellow boxes, also iron-backed boxes, and must be free of babbitt, also free of excessive grease and dirt.

9. **Cocks and Faucets.**—To be mixed red and yellow brass, free of gas cocks and beer faucets.

10. **Heavy Yellow Brass.**—May consist of heavy brass castings, rolled brass, rod brass ends, chandelier brass, tubing, not to contain over 15 per cent of tinned and/or nickel plated material; no piece to measure more than 12 inches over any one part and must be in pieces not too large for crucibles. Must be free of manganese mixture, condenser tubes, iron, dirt and excessive corroded tubing. Must be free of aluminum brass containing over 0.20% aluminum.

11. **Yellow Brass Castings.**—Shall consist of brass castings in crucible shape, that is, no piece to measure more than 12 inches over any one part; must be free of manganese mixtures, tinned and nickel plated material, and must be free of visible aluminum brass.

12. **Light Brass.**—May consist of miscellaneous brass, tinned or nickel plated that is too light for heavy brass, to be free of gun shells containing paper, ashes or iron, loaded lamp bases, clock works and automobile gaskets. Free of visible iron unless otherwise specified.

13. **Old Rolled Brass.**—May consist exclusively of old pieces of sheet brass and pipe free from solder, tinned and nickel plated material, iron, paint, and corrosion, ship sheathing, rod brass, condenser tubes and Muntz metal material.

14. **New Brass Clippings.**—Shall consist of the cuttings of new sheet brass to be absolutely clean and free from any foreign sub-

stances and not to contain more than 10 per cent of clean brass punchings to be not smaller than $\frac{1}{4}$ inch in diameter.

15. **Brass Pipe.**—Shall consist of brass pipe, free of nickel plated, tinned, soldered or pipes with cast brass connections. To be sound, clean pipes free of sediment and condenser tubes.

16. **No. 1 Red Composition Turnings.**—To be free of railroad car-box turnings and similarly excessively leaded material, aluminum, manganese and yellow brass turnings; not to contain over 2 per cent free iron; to be free of grindings and foreign material especially babbitt. Turnings not according to this specification, to be sold subject to sample.

17. **No. 1 Yellow Rod Brass Turnings.**—Shall consist of strictly rod turnings, free of aluminum, manganese, composition, Tobin and Muntz metal turnings; not to contain over 3% free iron, oil or other moisture; to be free of grindings and babbitts; to contain not more than 0.30% tin and not more than 0.15% combined iron.

18. **No. 1 Yellow Brass Turnings.**—Shall consist of yellow brass turnings, free of aluminum, manganese and composition turnings; not to contain over 3% of free iron, oil or other moisture; to be free of grindings and babbitts. To avoid dispute, to be sold subject to sample.

19. **Auto Radiators.**—All radiators to be subject to deduction of actual iron. The tonnage specification should cover the gross weight of the radiators.

20. **Pewter.**—Shall consist of table ware and soda fountain boxes, but in any case must test 84% tin. Syphon tops to be treated for separately.

21. **Zinc.**—Must consist of clean sheet and cast zinc, also cast batteries to be free of loose oxide and dross, salammoniac cans and other foreign materials.

22. **Zinc Dross.**—Must be unsweated in slabs and must contain a minimum of 92% of zinc.

23. **Tin Foil.**—Shall consist of pure foil free of lead composition and other foreign ingredients and matters.

24. **Electrotype Shells.**—Must be hand picked and free of loose dross and chunks of dross.

25. **Scrap Lead.**—Should be clean soft scrap lead.

26. **Battery Lead Plates.**—Shall consist of dry battery lead plates, moisture not to exceed 1 per cent, allowance to be made for wood, rubber and paper and excess moisture.

27. New Sheet Aluminum Clippings and New Aluminum Wire.—Shall consist of new sheet aluminum, cuttings and new aluminum wire. Must be free from oil, grease and any other foreign substance. Must be guaranteed not less than 98 per cent pure aluminum and not to contain more than 10 per cent of clean aluminum punchings to be not smaller than one-quarter inch in diameter.

28. Old Aluminum Wire.—Shall consist of old aluminum wire guaranteed 98 to 99 per cent pure aluminum and must be free from iron cores, insulation and any other foreign substances.

29. Alloy Sheet Aluminum.—To be sold on specification and sample.

30. Painted Sheet Aluminum.—Shall consist of painted sheet aluminum and must be absolutely free from iron, dirt or any other foreign substance.

31. Old Sheet Aluminum.—Shall consist of old and manufactured sheet aluminum. Must be free from painted sheet aluminum, iron, dirt and any other foreign substance.

32. Aluminum Castings.—Shall consist of aluminum castings, free from iron, babbitt, brass and any other foreign substance. Must not exceed 2 per cent of oil and grease. Free of pistons.

33. Aluminum Borings.—To avoid dispute, should be sold subject to sample.

34. Aluminum Foil.—Shall consist of Pure Aluminum Foil, free from paper and any foreign ingredients.

35. Babbitt Metal.—Shall contain bearing metal of all kinds. Shall not contain scrap hard metal, Allen metal (which is copper and lead alloy) die cast, zinc boxes or type metal.

36. Packages.—Shall be good strong packages suitable for shipment and each package shall be plainly marked with separate shipping marks and numbers and with the gross and tare weights, so that the packages may reach their destination and their weights can be easily checked.

CHAPTER XXVII

GERMAN TRADE SPECIFICATIONS FOR OLD METALS, METAL SCRAP, AND METAL INGOTS ¹

A. GENERAL CONDITIONS

§ 1. Delivery

The seller is entitled to deliver at contract price a quantity of $\frac{1}{2}$ per cent more or less of the weight agreed upon.

Expressions, such as "about," permit the delivery of 1 per cent more or less of the quantity sold at contract price.

In the case of metal ingots, the difference between sold and delivered quantity must not be above or below the weight agreed upon by the weight of one ingot of customary size.

The specification "from . . . to . . . kgs" gives the seller the option of delivery within these limits—including the limiting weights stated. Terms, such as "about," etc., are of no significance in this case.

§ 2. Claims

Material bought as inspected cannot be objected to later on account of apparent faults.

Material bought without previous inspection must be inspected and verified at the place of delivery immediately after arrival, as far as this is possible in the ordinary course of business. If forwarding instructions are promptly given by the buyer, inspection and verification may take place at destination of material even if transit is interrupted on the way.

§ 3. Payments

Payments must be made immediately after delivery and verification of goods, settlement for partial supplies to take place immediately after delivery and verification of each single consignment.

¹ In force since May, 1926.

B. SPECIAL CONDITIONS

§ 4. Copper

Firebox Copper shall consist of old, broken-up locomotive fire-boxes, and must not contain any manganese copper.

Material containing dirt, scale, or sediment can only be supplied if these impurities are removable by beating. Loss in weight caused by cleaning, if exceeding 0.25 per cent, goes to the charge of the seller, who in this case must also bear the cost of cleaning.

Crucible material must not contain pieces exceeding 25 cm. in length and 15 cm. in width.

Supplies must not contain more than 10 per cent of loose rivets and bolts.

Heavy Copper shall consist of old heavy copper (tubes and apparatus), thick copper segments, and new copper sheet cuttings. It must be essentially free from dirt and scale. Impurities exceeding 1 per cent, together with the costs of cleaning, go to the charge of the seller. Tinned material and parts containing lead solder connection are only permitted up to 10 per cent. Solder must be run off as far as technically possible.

If "untinned material" is specified, neither tinned material nor parts containing lead solder may be delivered.

Crucible material must not include pieces over 25 cm. long and 15 cm. broad. Old washing tubs, water kettles, domestic copper, bathing stoves may not be delivered as heavy copper.

Old electrolytic copper and electrolytic copper wire shall consist of pure electrolytic copper, free from tinned, armored, insulated, and enamelled material, and free from solder connections.

Well cleaned copper wire, insulation burned off, which is not brittle, may be delivered, excepting hair wire (wire thickness below 0.15 mm.).

Telephone Copper wire must show at least 98 per cent copper. It must be free from enclosures and should not contain armored or otherwise insulated wire. Loose, tangled, and dishevelled wire is not admissible.

Light Copper may contain copper utensils of every description, mixed copper wire, and light copper segments. One-third of the quantity delivered may be tinned material, but must be free from

iron. Solder parts must be sweated off. Electrotypes shells may not be included.

Copper Turnings shall consist of turnings of pure copper, not containing foreign substances.

Mechanical impurities, such as moisture and iron, are admitted in percentages of up to 5 per cent—of which 2 per cent may be iron. However, the seller has to pay for the percentages of impurities beyond 3 per cent.

§ 5. Zinc

Remelted Spelter (Remelted) must be supplied in regular plates, melted from old zinc, and showing at least 96 per cent zinc contents. Contents of iron and copper must not total more than $\frac{1}{2}$ per cent, while aluminum is admitted up to 0.25 per cent, copper, up to 0.30 per cent. The balance of impurities should consist chiefly of lead and tin.

Quality Zinc must assay at least 98 per cent. If a delivery is not up to the proper standard of 98 per cent purity, the buyer is not entitled to refuse acceptance provided the zinc contents do not drop below 97.50 per cent. The respective less-value, however, must be refunded, bonification not to exceed double the difference.

Other ingredients of quality zinc should consist mainly of lead. Insignificant percentages of iron, tin, copper, nickel, aluminum must be admitted, the percentage of iron not to exceed 0.25 per cent, tin 0.15 per cent, and other ingredients, 0.10 per cent each.

Old Zinc must not contain more than 1 per cent mechanical iron and 1 per cent clean tar zinc. Deliveries not showing more than 5 per cent mechanical iron and clean tar zinc combined must be accepted, however. Percentages of iron exceeding 1 per cent may be deducted from the weight. Clean tar zinc of more than 1 per cent is to be sorted out, and is subject to special agreements concerning price.

Corroded zinc from electrolytic batteries cannot be delivered.

The quantity of tarred zinc present must be ascertained before remelting the material. The weight of the mechanical iron contained is to be determined after melting.

The seller has the option to be represented by a sworn-in sampler during these proceedings.

New Zinc Sheet Cuttings must consist of new, clean, bright zinc sheet cuttings, free from soldered parts and mechanical foreign substances.

Zinc Fuses Alloy must consist of plates, ingots, fuse bodies or parts thereof. The alloy must contain at least 90 per cent of zinc, and not less than 3 per cent of copper. The percentage of aluminum present should not exceed 3 per cent, that of other ingredients, 2 per cent, of which $\frac{1}{2}$ per cent may be iron.

First Class Hard Spelter must consist of well-sounding plates or ingots, unburned and free from ashes. The weight of one ingot must not exceed 40 kg., and the zinc contents should be at least 90 per cent. The material must not contain any iron parts.

Zinc Foundry Ashes must assay at least 55 per cent zinc and not more than 20 per cent lead. Chlorine and sulphur must not exceed 2 per cent total, of which the sulphur is not to exceed 1 per cent.

Zinc Galvanizing Ashes from galvanizing works shall assay at least 63 per cent, and must not contain more than 6 per cent chlorine and 6 per cent lead.

Sal-Ammoniac Zinc Skimmings from Galvanizing Works. Only dry, non-deliquested material may be delivered. The assay must show at least 46 per cent zinc.

§ 6. Lead, Tin, Aluminum

Lead Scrap is to consist chiefly of articles and scrap made of soft lead. Up to about 15 per cent of the weight of the delivery may consist of waste pipes and lead foil, the latter not exceeding 5 per cent. Antimonial lead up to 3 per cent is admitted. Adhesive impurities may be deducted from the weight if their quantity exceeds 2 per cent.

Soft Lead Scrap must consist of old lead articles testing at least 99 per cent pure lead. Adhesive dirt up to 2 per cent must be tolerated. Any admixtures of lead alloy, no matter what compounds, may not be delivered.

Battery Lead is to consist essentially of battery lead plates, assaying at least 80 per cent lead in the original material.

Lead Ingots must assay at least 97 per cent lead. Other ingredients may be tin, antimony, copper, and zinc. Copper and zinc contents combined must not exceed 0.75 per cent.

Pewter is to contain articles assaying at least 75 per cent tin. Twenty-five per cent of the weight of the delivery may consist of articles made of britannica tin. Tankard tops with joints can only be delivered provided the joints show the above indicated tin contents.

Domestic Tin (Kleinzinn) shall consist of articles testing 50 per cent tin—average. Spoons and forks with iron insides cannot be supplied.

Spoons and Forks Tinto consist of tin forks and spoons with iron insides. Handles alone cannot be delivered.

Tin Alloy must be a metallurgically produced tin-lead alloy assaying at least 54.40 per cent tin. Antimony up to 3.60 per cent, and copper up to 0.15 per cent must be admitted. The material must be technically free from iron, arsenic, and zinc.

Remelted Pure Aluminum, which is sold as 98/99 pure, must show at least the guaranteed minimum purity of 98 per cent. Iron contents of up to 1 per cent are not objectionable.

Aluminum Alloy above 92 per cent purity. All deliveries of this material in grades of 95 per cent and up must show the agreed minimum contents of aluminum, or a toleration of 0.5 per cent aluminum granted. The iron contents must not exceed 1.25 per cent.

Aluminum Alloys in grades of 88 per cent, and up to 92 per cent. Unless a minimum content has been specially agreed upon, deliveries may show a deficit in aluminum contents of up to 0.50 per cent, the remainder to consist chiefly of zinc, copper, and tin. The following limits for other ingredients must not be exceeded: iron 1.5%, silicon 1%, manganese 0.50%, magnesium 0.25%, lead 0.25%, nickel 0.20%.

Aluminum Alloys in grades of 85 to 88 per cent purity may assay up to 1 per cent less, unless minimum contents have been specially agreed upon. The balance should mainly consist of zinc, copper, and tin. The following limits for other ingredients must not be exceeded: Iron 2%, silicon 1.5%, lead 0.5%, manganese 0.5%, magnesium 0.3%, nickel 0.2%.

New Pure Aluminum Sheet Clippings must be delivered unlacquered, clean, free from oxidation and from all foreign materials. It should not contain aluminum foil. Aluminum wire of 98/99 purity may be included up to 20 per cent of the quantity supplied, provided the wire is not oxidized, dirty, or contaminated with solder. Hair wire, that is to say, wire gauging under 0.15 mm., may not be delivered.

Aluminum Motor Castings. Any foreign adhesive metals, such as iron, brass (yellow brass), and gunmetal (red brass) must be removed. Regarding injurious ingredients in the alloy, the specifications made for ingots are to be applied.

Impurities, such as dirt and oil, to the total of 2 per cent are

admissible. Allowance must be granted for impurities above 2 per cent up to 5 per cent.

Aluminum Utensils (Geschirr Aluminium) shall consist of utensils made of sheets assaying 98/99 per cent aluminum. The material must be well cleaned. The seller must remove insulation, wood, and iron parts.

Aluminum Alloy Borings must not be oxidized and free from mechanical impurities, especially iron, electron, and magnesium. The borings must not contain mechanical iron above 6 per cent, and oil above 2 per cent. Regarding other detrimental ingredients, the rules given under aluminum ingots are to be applied.

§ 7. Gunmetal (*Red Brass*)

Preliminary Remarks. Ten per cent of the tin contents of gunmetal may be allowed for antimony and added to tin contents in all gunmetal and bronze materials.

Gunmetal Scrap (machinery gunmetal) shall consist of castings assaying 85 per cent copper plus tin.

Tin contents must not drop below 4 per cent, while the copper should not be less than 78 per cent. The balance may be made up by zinc and lead.

The lead contents must not exceed 5 per cent. Other ingredients are not to exceed 2 per cent, with the exception of zinc.

Iron must be allowed in percentages of up to 0.40 per cent. Detrimental contents of manganese, aluminum, and silicon in the alloys are not permissible.

Crucible material only and pieces not over 35 kg. in weight may be delivered.

American carboxes and spindle gunmetal are to be excluded from gunmetal scrap.

Locomotive and Railway Gunmetal must consist of machinery parts from locomotives and cars of the German railways. It must not contain bends (Kruemmer), door handles, fittings, etc. Adhesive white metal (babbitt) must be thoroughly melted off. Railway gunmetal originated from other countries may only be supplied if expressly specified as of foreign origin and provided its quality is at least equal to that of German railway gunmetal.

Marine Gunmetal must consist of casting parts from ships, assaying 80 per cent copper plus tin. Minimum copper contents are 74 per

cent, minimum tin contents, 4 per cent. The balance must consist chiefly of zinc.

The alloys may contain not more than 3 per cent of lead, the other uninjurious ingredients not exceeding 3 per cent.

Detrimental contents of aluminum, manganese, and iron are inadmissible.

Marine gunmetal must be of crucible size and may not contain pieces exceeding 35 kg. in weight.

Admiralty Bronze is to consist of casting parts from ships, assaying at least 92 per cent copper plus tin. Material containing 90 per cent copper plus tin cannot be rejected, but the less-contents must be bonified according to deviations (pro rata). The remainder of the alloying constituents must consist chiefly of zinc. Contents of lead up to 2 per cent cannot be objected to. Detrimental ingredients of aluminum, manganese, silicon, and iron are not admissible.

Admiralty bronze must be supplied in sizes suitable for furnace treatment.

Gunmetal Borings not sold subject to sample, origin, or analysis must assay at least 80 per cent copper plus tin, at a minimum of 74 per cent copper and 4 per cent tin. The balance must chiefly be zinc. A toleration up to 5 per cent must be granted for lead.

A detrimental content of manganese, aluminum, silicon, and iron in the alloy is not admissible. Iron contents exceeding 0.40 per cent are to be considered detrimental.

Mechanical iron up to 3 per cent cannot be objected to. Regarding deliveries containing from 3 to 5 per cent iron turnings, the seller is under obligation to refund the less-value.

Gunmetal turnings bought subject to sample or analysis may show a variation of copper and tin contents of 1 per cent between the sample or analysis and the material delivered.

Bronze Wire Cloth (bronze wire gauze) shall consist of clean, smooth wire gauze in rolls. The wire gauze may be made of different thicknesses of wire. The length wire must be of bronze, cross wires may be of brass. The material must be free from dirt and solder connections. Wire netting with a third thread of wire interwoven may be supplied up to 20 per cent of the total quantity delivered, granting a bonification of 5 per cent of the weight of these special wire nettings.

If unclean bronze wire gauze in pieces has been sold subject to sample delivery, sample may vary to the extent of 2 per cent from

the material actually delivered. Small quantities of solder connections may be included.

Gunmetal Ingot 85/5 must assay at least 90 per cent copper plus tin plus antimony, of which 84 per cent must be copper, and 5 per cent tin plus antimony. Up to 1 per cent antimony, 3 per cent lead, and 10 per cent zinc may be tolerated.

Iron contents up to 0.40 per cent must be tolerated.

A detrimental contents of manganese, aluminum, silicon, and sulphur in the alloy is not admissible.

Railway Gunmetal Ingots must comply with the specifications of the German Railway Authorities (E. Z. A.).

Bronze 90/10 with a toleration of 3 per cent must assay at least 97 per cent copper plus tin plus antimony, and contain not less than 87 per cent copper and at least 9 per cent tin plus antimony. Of other ingredients not more than 1 per cent antimony, 1.50 per cent lead, 0.25 per cent iron, and 3 per cent zinc may be admitted.

The alloy must not show injurious ingredients of manganese, aluminum, silicon, and sulphur.

Bronze 80/20 with a toleration of 4 per cent must assay at least 96 per cent copper plus tin plus antimony, and contain at least 18 per cent tin plus antimony, 10 per cent of the tin contents must be allowed for antimony and to be reckoned as tin.

Other ingredients must not exceed: lead, 3 per cent; zinc, 4 per cent; iron, 0.30 per cent.

The alloy must not contain any injurious ingredients of manganese, aluminum, silicon, and sulphur.

§ 8. Brass (*Yellow Brass*).

Heavy Brass (Castings) shall consist mainly of brass casting parts, thick sheet cuttings, and tube cuttings. The material is to be free from iron parts. The pieces must be of crucible size not exceeding 25 kg. in weight. The material must assay at least 60 per cent copper and 34 per cent zinc (average). Lead solder and lead must be carefully sweated off.

Uninjurious ingredients in amounts of up to 6 per cent must be tolerated.

The alloy must not show detrimental percentages of aluminum, manganese, and iron. Delta and other special alloys cannot be supplied.

Up to 10 per cent of delivery may consist of brass rods and fuses.

Nickel plated and tinned parts must not exceed 10 per cent of the quantity delivered.

New Brass Sheet Clippings shall consist of clippings originating from soft and hard rolled sheet brass. Up to 10 per cent of the delivered quantity may consist of punchings.

The material must be new, clean, and free from solder, and must not contain galvanized, tinned, nickel plated, or oxidized parts.

The alloy is to show at least 62 per cent copper, besides zinc, and must be free from detrimental percentages of aluminum, lead, iron, manganese, nickel, and tin.

New Hard Brass Sheet Cuttings must consist of new, clean, cuttings originating from rolled brass sheets. The cuttings must be free from solder and may not contain galvanized, tinned, nickel-plated, and oxidized parts.

The alloy must show a minimum of 57 per cent copper, besides zinc. Foreign ingredients should not exceed 3.50 per cent, with not more than 3 per cent lead. Detrimental percentages of tin, aluminum, lead, iron, manganese, and nickel are not admitted.

The quantity of punchings must not exceed 10 per cent of delivery. Delta, Durana, and other special alloys cannot be supplied as brass sheet cuttings. Cuttings from sheets used in the manufacture of harmonicas, and cuttings from tuning sheets of musical instruments must be specified as such.

Light Brass consists of old brass articles which may be tinned, soldered, and galvanized. The material must be free from iron as far as possible. Adhesive iron, difficult to remove, cannot be objected to if it does not exceed 5 per cent. Any excess of iron up to 8 per cent, together with costs of removing, must be refunded.

Brass radiators can only be delivered after solder has been sweated off.

Brass Rod Turnings (Messingschrauben-Späne) shall assay at least 57 per cent copper in the dry material, free from iron. The balance is to be chiefly zinc. Deliveries must not show detrimental contents of tin, aluminum, lead, iron, and manganese in the alloy.

Contents of mechanical iron and moisture of 4 per cent total is allowed, iron not to exceed 1 per cent. Material with a combined contents of 6 per cent mechanical iron and moisture must be accepted subject to bonification of the excess (beyond 4 per cent).

Delta, Durana, and other special alloys must not be delivered.

Brass Rod Ends shall consist of new brass rod ends from brass rod manufacturers. The material must assay at least 57 per cent copper, balance to be zinc. The alloy must not contain injurious contents of tin, aluminum, iron, and manganese.

Brass Tubes must neither be tinned nor corroded. Dirt and sediment has to be removed as far as possible. No claim may be made on account of dirt and sediment not exceeding 2 per cent. Further impurities up to 5 per cent are subject to bonification, together with the costs of cleaning. Condenser tubes may only be included if they are practically free from tin.

Regarding tin tubes, the above rules are to apply correspondingly.

Rifle Shells have to be drawn out of one piece. Material must be essentially clean, exploded, and free from powder and iron. No griddled shells, or appreciably oxidized, corroded, or dirty material may be delivered. Shells damaged by explosion are to be excluded.

Rem. muffled shells are to be specified as such.

Brass Cartridge Cases must be drawn out of one piece. The material must be essentially clean, and free from powder, iron, and primers. Muffled shells or appreciably oxidized material are not deliverable. Corroded shells or material damaged by fire, or cases containing impurities cannot be delivered.

Brass Fuses (Artillery Brass) must be delivered free from powder, iron, and aluminum parts. The alloy may not contain manganese and detrimental percentages of aluminum.

High-class Brass Ingots shall assay at least 64.50 per cent copper, balance to consist of zinc. The total of foreign ingredients in the alloy may not exceed 5 per cent. The iron contents must not exceed 1 per cent, the lead contents, 2.5 per cent. Injurious percentages of aluminum, manganese, and nickel are not admissible. High-class brass ingots must show a greenish yellow color when filed.

Tombac Cuttings. Only new, ungalvanized cuttings, free from soldered parts may be delivered. The assay must show at least 84 per cent copper, rest to be chiefly zinc. The alloy must not contain any injurious contents of aluminum, lead, iron, manganese, nickel, and tin.

§ 9. German Silver.

First-class German Silver Sheet Cuttings shall consist of new cuttings, free from dirt and soldered parts. The alloy must contain a minimum of 50 per cent copper and 12 per cent nickel, balance to consist chiefly of zinc. Foreign uninjurious ingredients are permis-

sible up to 1 per cent. The contents of lead, tin, and iron must not exceed 0.50 per cent each.

Old German Silver Scrap shall consist of parts of utensils made of German silver. Adhesive foreign materials up to 5 per cent cannot be objected to.

German Silver Ingots. The ingots must be free from aluminum and manganese and must assay at least 50 per cent copper and 12 per cent nickel. Contents of iron may not exceed 1 per cent. Foreign uninjurious ingredients should not be present in quantities above 3 per cent.

Old Cupro-nickel Jackets must be delivered free from iron and aluminum. Only such material may be termed clean and well melted-out, which does not contain more than 5 per cent lead. Deliveries containing lead up to 8 per cent, may not be refused, but give the buyer the privilege of demanding bonification for less-value for the lead contents above 5 per cent.

§ 10. White Metal.

First Quality White Metal must assay at least 79 per cent tin. The average contents of lead must not surpass 3.50 per cent, that of copper, 7 per cent. The balance should consist chiefly of antimony. Zinc up to 0.20 per cent is admissible. The alloy must not contain mercury and aluminum.

First-class White Metal Borings must consist of an alloy showing a minimum tin content of 79 per cent. The average lead contents should not exceed 3 per cent, those of copper, 7 per cent. The remainder should chiefly consist of antimony. Zinc is admissible in quantities of up to 0.20 per cent. The alloys must not contain mercury or aluminum. Admixtures of mechanical iron, oil, dirt, etc., up to 2 per cent must be tolerated, while higher percentages are subject to bonification by the seller.

Deliveries of white metal borings, sold subject to sample, must not vary more than one unit each for tin, copper, and antimony as compared with the sample. The lead contents may show variations of up to 5 per cent. Deviations in the percentage of mechanical impurities contained are subject to bonification by the seller.

Mixed white metal and gun metal borings sold subject to sample, may show a deviation of 2 per cent in the percentage of white metal to gun metal borings between sample and delivery. Any excess over 2 per cent up to 6 per cent is to be made good by the seller.

TABLE 44.—MELTING AND BOILING POINTS OF METALS

Metal	Melting point, degrees C.	Boiling point, degrees C.
Aluminum.....	658.7	1800.0
Antimony.....	630.0	1460.0
Arsenic.....	850.0	450.0 (Sublimes)
Barium.....	850.0	
Bismuth.....	271.0	1440.0
Boron.....	2350.0	3500.0 (Sublimes)
Cadmium.....	320.9	778.0
Calcium.....	810.0	
Cerium.....	623.0	
Chromium.....	1520.0 to Fe	2200.0
Cobalt.....	1610.0	
Copper.....	1083.0	2100.0
Gold.....	1063.0	2100.0
Iron.....	1530.0	2450.0
Lead.....	327.4	1525.0
Magnesium.....	651.0	1120.0
Manganese.....	1260.0±20	1900.0
Mercury.....	-38.87	357.0
Molybdenum.....	2550.0	3350.0
Nickel.....	1452.0	2450.0
Phosphorus.....	44.1	287.0
Platinum.....	1755.0	2650.0
Potassium.....	62.3	667.0
Radium.....	900.0	
Selenium.....	218.5	690.0
Silicon.....	1420.0	3800.0
Silver.....	961.0	1955.0
Sodium.....	97.5	742.0
Strontium.....	<Ca and Ba	
Sulphur.....	118.0	444.5
Tin.....	231.9	2270.0
Titanium.....	1795.0	2700.0
Tungsten.....	3267.0	3700.0
Uranium.....	Near Mo.	3100.0
Vanadium.....	1720.0	
Zinc.....	419.4	918.0
Zirconium.....	1700.0 (?)	

TABLE 45.—INTERNATIONAL ATOMIC WEIGHTS OF METALS (1922)

Metal	Symbol	Weight	Metal	Symbol	Weight
Aluminum.....	Al	27.0	Molybdenum.....	Mo	96.0
Antimony.....	Sb	120.2	Nickel.....	Ni	58.68
Arsenic.....	As	74.96	Phosphorus.....	P	31.04
Barium.....	Ba	137.37	Platinum.....	Pt	195.2
Bismuth.....	Bi	209.0	Potassium.....	K	39.10
Boron.....	B	10.9	Radium.....	Ra	226.0
Cadmium.....	Cd	112.4	Selenium.....	Se	79.2
Calcium.....	Ca	40.07	Silicon.....	Si	28.1
Cerium.....	Ce	140.25	Silver.....	Ag	107.88
Chromium.....	Cr	52.0	Sodium.....	Na	23.00
Cobalt.....	Co	58.97	Strontium.....	Sr	87.63
Copper.....	Cu	63.57	Sulphur.....	S	32.06
Gold.....	Au	197.2	Tin.....	Sn	118.7
Iron.....	Fe	55.84	Titanium.....	Ti	48.1
Lead.....	Pb	207.20	Tungsten.....	W	184.0
Magnesium.....	Mg	24.32	Uranium.....	U	238.2
Manganese.....	Mn	54.93	Vanadium.....	V	51.0
Mercury.....	Hg	200.6	Zinc.....	Zn	65.37

TABLE 46.—SPECIFIC HEATS OF IMPORTANT METALS

At about 15° C.

Aluminum.....	0.167
Antimony.....	0.048
Arsenic.....	0.076
Bismuth.....	0.030
Cadmium.....	0.054
Copper.....	0.086
Gold.....	0.030
Iron.....	0.116
Silver.....	0.055
Tin.....	0.055
Zinc.....	0.093

TABLE 47.—SPECIFIC GRAVITIES OF LEAD-TIN ALLOYS

Per cent of tin	Specific gravity	Determined by	Per cent of tin	Specific gravity	Determined by
0	11.376	Long	36.22	9.458	Calvert
8.5	10.815	Long	52.7	8.779	Long
10.20	10.751	Calvert	53.18	8.774	Calvert
12.2	10.590	Long	63.01	8.418	Calvert
12.43	10.587	Calvert	69.0	8.188	Long
15.91	10.421	Calvert	69.43	8.196	Calvert
21.8	10.080	Long	73.97	8.093	Calvert
22.11	10.105	Calvert	77.00	7.927	Long
35.8	9.460	Long	100.00	7.294	Long

TABLE 48.—SPECIFIC GRAVITIES OF LEAD-ANTIMONY ALLOYS

Per cent of antimony	Specific gravity	Determined by	Per cent of antimony	Specific gravity	Determined by
0	11.376	Matthiessen	23.68	9.723	Calvert
2.3	11.194	Matthiessen	37.1	8.989	Matthiessen
5.5	10.930	Matthiessen	38.39	8.953	Calvert
10.5	10.586	Matthiessen	54.1	8.201	Matthiessen
11.08	10.556	Calvert	55.47	8.330	Calvert
13.48	10.387	Calvert	65.14	7.830	Calvert
16.4	10.144	Matthiessen	71.36	7.525	Calvert
17.30	10.136	Calvert	75.69	7.432	Calvert
22.7	9.811	Matthiessen	100.00	6.713	Matthiessen

TABLE 49.—COLOR SCALE

	Degrees C.	Degrees F.
Lowest visible red in a dark room.....	470	880
Incipient redness.....	525	980
Dark red.....	550- 625	1020-1040
Blood red.....	650- 700	1200-1290
Dark cherry red.....	750- 800	1380-1470
Cherry red.....	850- 900	1530-1650
Light cherry red.....	900- 950	1650-1740
Dark orange.....	975-1025	1790-1880
Light orange.....	1050-1100	1920-2010
Yellow.....	1125-1200	2050-2190
White.....	1250	2280

The estimation of temperatures by colors depends largely upon individual judgment, of course, and is rarely uniform with two observers. The appearance of the colors is governed not only by the susceptibility of the eye, but by the brightness of the sunlight, the degree of illumination, and by the radiation of the heated body.

TABLE 50.—SEGER CONES—NEW SERIES

Cone Number	Melting point, degrees C.	Cone Number	Melting point, degrees C.	Cone Number	Melting point, degrees C.
022	600	02a	1060	19	1520
021	650	01a	1080	20	1530
020	670	1a	1100	26	1580
019	690	2a	1120	27	1610
018	710	3a	1140	28	1630
017	730	4a	1160	29	1650
016	750	5a	1180	30	1670
015a	790	6a	1200	31	1690
014a	815	7	1230	32	1710
013a	835	8	1250	33	1730
012a	855	9	1280	34	1750
011a	880	10	1300	35	1770
010a	900	11	1320	36	1790
09a	920	12	1350	37	1825
08a	940	13	1380	38	1850
07a	960	14	1410	39	1880
06a	980	15	1435	40	1920
05a	1000	16	1460	41	1960
04a	1020	17	1480	42	2000
03a	1040	18	1500		

TABLE 51.—CONVERSION OF THERMOMETER READINGS

Degrees C.	Degrees F.	Degrees C.	Degrees F.	Degrees C.	Degrees F.
-30	-22	200	392	650	1202
-25	-13	210	410	675	1247
-20	- 4	220	428	700	1292
-15	+ 5	230	446	725	1337
-10	14	240	464	750	1382
- 5	23	250	482	775	1427
0	32	260	500	800	1472
5	41	270	518	825	1517
10	50	280	536	850	1562
15	59	290	554	875	1607
20	68	300	572	900	1652
25	77	310	590	925	1697
30	86	320	608	950	1742
35	95	330	626	975	1787
40	104	340	644	1000	1832
45	113	350	662	1025	1877
50	122	360	680	1050	1922
55	131	370	698	1075	1967
60	140	380	716	1100	2012
65	149	390	734	1125	2057
70	158	400	752	1150	2102
75	167	410	770	1175	2147
80	176	420	788	1200	2192
85	185	430	806	1225	2237
90	194	440	824	1250	2282
95	203	450	842	1275	2327
100	212	460	860	1300	2372
110	230	470	878	1400	2552
120	248	480	896	1500	2732
130	266	490	914	1600	2912
140	284	500	932	1700	3092
150	302	525	977	1800	3272
160	320	550	1022	1900	3452
170	338	575	1067	2000	3632
180	356	600	1112		
190	374	625	1157		

TABLE 52.—WEIGHTS OF VARIOUS MATERIALS *

	Average per cubic foot, pounds
Brick:	
Common red brick	100.0
Fire clay	125 to 140
Silica brick	105.0
Chrome brick	175
Magnesia brick	170.0
Cement:	
Portland cement	78.0
Hydraulic cement	60.0
Fine ground clays, silica, cement, etc.:	
Fire clay	85.0
Silica cement	75.0
Magnesia cement	127.0
Chrome cement	135.0
Grain magnesite (as shipped)	112.0
Coal and coke:	
Anthracite	60.0
Bituminous coal	49.0
Charcoal	18.5
Coke	26.3
Concrete:	
Cement, fine	137.0
Rubble, coarse	119.0
Earth:	
Loam, dry, loose	76.0
Loam, packed	95.0
Loam, soft, loose mud	108.0
Loam, dense mud	125.0
Glass:	
Common window glass	157.0
Plate glass	172.0
Flint glass	192.0
Floor or skylight glass	158.0
Lime:	
Quick, loose lumps	53.0
Quick, fine	75.0
Stone, large rocks	168.0
Stone, irregular lumps	96.0
Masonry:	
Granite or limestone	165.0
Mortar, rubble	154.0
Dry Masonry	138.0
Sandstone, dressed	144.0

*Courtesy of Harbison Walker Refractories Co.

TABLE 52.—*Continued*

	Average per cubic foot, pounds
Metals:	
Aluminum.....	166.0
Brass, cast.....	524.0
Bronze.....	534.0
Copper, cast.....	537.0
Copper, rolled or wire.....	555.0
Iron, cast.....	450.0
Iron, wrought.....	482.0
Lead, cast.....	708.0
Lead, rolled.....	711.0
Steel, cast.....	490.0
Steel, rolled.....	495.0
Tin, cast.....	459.0
Zinc, cast.....	438.0
Oils:	
Engine oil.....	55.0
Crude oil.....	48.0
Petroleum.....	55.0
Gasoline.....	43.0
Rock:	
Chalk.....	145.0
Granite.....	165.0
Gypsum.....	143.0
Sandstone.....	144.0
Pumice stone.....	57.0
Quartz.....	165.0
Salt, coarse.....	45.0
Salt, fine.....	49.0
Shales.....	162.0
Slate, American.....	175.0
Sand:	
Dry and loose.....	100.0
Dry and packed.....	110.0
Wet and packed.....	130.0
Gravel, packed.....	118.0
Water:	
Water as ice.....	58.7
Water at 32° F.....	62.4
Water at 212° F.....	59.6
Woods, dry:	
Apple.....	48.0
Beech.....	43.0
Birch.....	45.0
Cedar, American.....	35.0

TABLE 52.—*Continued*

	Average per cubic foot, pounds
Woods, dry:— <i>Continued</i>	
Chestnut.....	41.0
Ebony.....	76.0
Elm.....	35.0
Hemlock.....	25.0
Hickory.....	53.0
Ironwood.....	114.0
Mahogany.....	35 to 53
Maple.....	49.0
Oak, live.....	59.0
Oak, white.....	50.0
Pine, white.....	25.0
Pine, yellow northern.....	34.0
Pine, yellow southern.....	45.0
Spruce.....	25.0
Walnut.....	35.0

TABLE 53.—IMPORTANT FURNACE CONSTRUCTION DATA *

- 1 square foot $4\frac{1}{2}$ -in. wall requires 7 nine-inch straight brick.
- 1 square foot 9-in. wall requires 14 brick.
- 1 square foot $13\frac{1}{2}$ -in. wall requires 21 brick.
- 1 cubic foot of brickwork requires 17 brick.
- 1 cubic foot of fire-brickwork weighs 125 to 140 pounds.
- 1000 brick (closely stacked) occupy 56 cubic feet.
- 1000 brick (loosely stacked) occupy 72 cubic feet.
- From 400 to 600 pounds of fire clay are enough to lay one thousand brick. Finely ground fire clay should be used for laying up fire clay brick.

* Courtesy of Harbison Walker Refractories Co.

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